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AND TECHNOLOGY

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Meeting		City	Hotel	Date
1960	Fall	New York	Commodore	September 13–16
1961	Spring	Louisville	Brown	April 18–21
1961	Fall	Chicago	Sherman	September 5–8
1962	Spring	Boston	Statler	April 24–27
1962	Fall	Cleveland	Cleveland	October 16–19
1963	Spring	Toronto	Royal York	May 7–10
1963	Fall	New York	Commodore	September 10–13
1964	Spring	Detroit	Cadillac	April 28–May 1
1964	Fall	Chicago	Sherman	September 1–4

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NEW BOOKS AND OTHER PUBLICATIONS

INTRODUCTION TO RUBBER TECHNOLOGY. Edited by Maurice Morton. Published by Reinhold Publishing Corp., 430 Park Avenue, New York 22, New York. Hard cover, 6 × 9 inches, 547 pages. Price: $10.00.—This basic text on rubber technology marks the culmination of a notable educational campaign launched about four years ago by the ACS Division of Rubber Chemistry jointly with the various Rubber Groups throughout the country. Dr. Morton has done an excellent job of selecting the twenty papers which cover a rapidly growing technology logically and comprehensively. New members of the industry are fortunate to have the subject presented to them in elementary terms by these experts, while others should welcome the volume as a reference work or a refresher course. The introductory tone of the compendium was maintained by excluding advanced lecture material presented in the program and by having each of the contributions begin with a definition of basic terminology. Photographs, tables, graphs and an index enhance the text's value. [From a review in *Rubber Age.*]

"Introduction to Rubber Technology" represents one of the many traditional activities of the Division of Rubber Chemistry of the American Chemical Society. It is also the direct result of the growing educational activities of the various active Rubber Groups in the United States. With the advent of the synthetic rubbers and allied synthetic polymers, the rubber industry found itself more and more involved in "chemical" fields. There resulted a growing demand, on the part of the technologist as well as from others in the sales, service, and purchasing activities, for more technical information about these expanding fields. Hence various Rubber Groups in all parts of the country began sponsoring lecture series on rubber technology for the benefit of their members and the industry as a whole. In the Fall of 1956, the editor of the proposed book was appointed by the Division Chairman, with instructions to select the most suitable of the available lectures as material for inclusion in the book. The various Rubber Groups were then asked to submit their collected lectures, and, in due course, material was available from the following Groups:

Akron	Detroit
Boston	New York
Buffalo	Philadelphia
Chicago	Rhode Island
Connecticut	Southern Ohio

The chapters which stemmed from these lectures are as follows: 1. History and Summary of Rubber Technology, B. S. Garvey, Jr., Pennsalt Chemicals Corporation. 2. Introduction to Polymer Chemistry, Maurice Morton, University of Akron. 3. Natural Rubber, Otis D. Cole, Firestone Tire and Rubber Company. 4. Vulcanization, L. E. Oneacre, Cooper Tire and Rubber Company. 5. Accelerators of Vulcanization, B. S. Garvey, Jr., Pennsalt Chemicals Corporation. 6. Antioxidants and Antiozonants, R. R. Barnhart and T. H. Newby, Naugatuck Chemical. 7. Rubber Plasticizers, Softeners, and Extenders, F. M. McMillan, Shell Chemical Corporation. 8. Carbon Black, John W. Snyder and Milton H. Leonard, Columbian Carbon Company. 9. Nonblack Compounding Ingredients, Ralph F. Wolf, Columbia-Southern Chemical Corporation. 10. Butadiene-Styrene Rubbers, J. D. D'Ianni, The Goodyear Tire and Rubber

Company. 11. Nitrile and Polyacrylate Rubbers, George A. Daum, B. F. Goodrich Chemical Company. 12. Butyl Rubber, W. L. Dunkel, R. F. Neu, and R. L. Zapp, Enjay Laboratories. 13. Neoprene, J. P. Munn, E. I. de Pont de Nemours & Company, Inc. 14. Hypalon Synthetic Rubber, F. Wayne Keeley, E. I. du Pont de Nemours & Company, Inc. 15. Polysulfide Polymers (Thiokol), J. S. Jorczak, Thiokol Chemical Corporation. 16. Silicone Rubbers, J. C. Montermoso, Quartermaster Research and Development Center. 17. Reclaimed Rubber, J. M. Ball, Midwest Rubber Reclaiming Company. 18. Latex, Sponge, and Foam, G. G. Winspear and R. R. Waterman, R. T. Vanderbilt Company. 19. Physical Testing, A. E. Juve, The B. F. Goodrich Research Center. 20. Processing Equipment, D. C. Chase, Farrel-Birmingham Company, Inc.

BIBLIOGRAPHY OF RUBBER LITERATURE FOR 1952-54. Edited by M. E. Lerner. Published by the Division of Rubber Chemistry, American Chemical Society, Akron, Ohio. Cloth cover, 6 × 9 inches, 793 pages. Price: $7.50.—This tenth edition of the Rubber Bibliography is the third one to be issued spanning a three-year period. It reflects the tremendous increase in literature and patents pertaining directly to rubber in all of its manifold ramifications. It contains 9169 references, against 6412 in the previous edition, representing an increase of 43 per cent.

This Bibliography is based on rubber references prepared at the United States Rubber Company, plus additional references culled from *Rubber Abstracts*, the journal published by the Research Association of British Rubber Manufacturers. Another source of information is *Revue générale du caoutchouc*, the journal published by the French Rubber Institute. Some references are based on bulletins prepared by the B. F. Goodrich Company, the full use of which will be reflected in the next edition, covering the 1955-56 period.

The letter-number identification system originally conceived by Donald E. Cable, United States Rubber Company, has been continued; while the journal abbreviations used, with a few exceptions, follow those established by the American Chemical Society. [Reviewed in *Rubber World*.]

LINEAR AND STEREOREGULAR ADDITION POLYMERS: POLYMERIZATION WITH CONTROLLED PROPAGATION (POLYMER REVIEWS, VOLUME 2). By Norman G. Gaylord and Herman F. Mark. Published by Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, New York. Hard cover, 6 × 9 inches, 571 pages. Price: $17.50.—In view of the accomplishments of the authors as writers and lecturers on polymerization, it is not surprising that this timely book is a useful one, especially to polymer research workers and experts who find it impossible to read the extraordinary volume of current literature. However, parts of the book are highly controversial and it has a number of limitations due to the nature of the subject matter, and apparently to the limited time and attention which the authors have been able to devote to the manuscript. The book is most useful for its many up-to-date references to recent art, theory, and conjecture in olefin polymerization, but it is often misleading with regard to historical and industrial aspects, especially by omissions and by order of presentation.

Although the book is devoted in large part to the polymerization processes, there are valuable discussions of polymer properties, including five tables bringing together specific gravities, transition temperatures, and other physical properties which have been reported for stereoregular polymers. The book

emphasizes the so-called Ziegler-type catalysts and their applications in polymerization of ethylene. However, the English free radical process which is commercially important for the preparation of high density polyethylenes is not discussed. Readers will appreciate that Gaylord and Mark have handled a difficult assignment and given us a useful volume which, however, must not be considered the last work in this rapidly growing field. [Condensed from a review by C. E. Schildknecht in *Journal of Polymer Science*.]

POLYMERS AND RESINS. THEIR CHEMISTRY AND CHEMICAL ENGINEERING. By Brage Golding. Published by Van Nostrand, New York. Hard cover, 6 × 9 inches, 744 pages. Price: $15.00.—This is a well-written painstaking attempt to produce a college textbook, "not a treatise," with comprehensive coverage of both the theory and the technology of polymeric and resinous substances. However, the technology of high polymers is by itself of such enormous scope that it stubbornly resists efforts to compress it within the confines of a single volume of "textbook" size. In addition, the science of materials has grown so important that the undergraduate's time and thought must be directed to learning not *how* materials behave but rather *why* they behave as they do. On the other hand, much of this information might be useful to an engineer, researcher, technician, salesman, or executive connected with the high polymer industries.

Considered in this light, the book under review, although carefully and often meritoriously written, is neither college text nor technological reference book, although part of each. Of roughly 700 pages about 500 represent technology, unbalanced and incomplete in that it is heavily weighted with resins and plastics but light on fibers, adhesives, and elastomers. Of greater significance are the 200 pages of high polymer theory, in the main solidly written. [Condensed from the review by A. X. Schmidt in *Journal of Polymer Science*.]

TECHNIQUES OF POLYMER CHARACTERIZATION. Edited by P. W. Allen. Published by Academic Press, Inc., 111 Fifth Avenue, New York 3, New York. Hard cover, 8½ × 5½ inches, 256 pages. Price: $9.50.—This collection by eight English scientists and industrial chemists fills a growing need for a critical, up-to-date evaluation of the more important techniques used to characterize high polymers. It represents a valuable addition to the recent number of excellent books on the physics and chemistry of high polymers which were generally restricted to theoretical rather than practical laboratory aspects of the subject. The editor has done well in keeping theoretical discussions to a minimum and by concentrating on a small number of techniques of proven reliability.

Following an introduction on solvents and the preparation of polymer solutions, these topics are covered: (1) Fractionation of High Polymers, (2) Number-Average Weights by Osmometry, (3) Other Methods for the Determination of Number-Average Molecular Weights, (4) Light-Scattering Techniques, (5) Viscometry, (6) Techniques of End-Group Analysis, and (7) Characterization of Block and Graft Copolymers.

The book was designed primarily for the graduate chemist familiar with the major works on the subject, but without practical experience in handling and performing measurements on polymeric substances. It has achieved this purpose admirably, and should prove equally useful to the more experienced worker who wants to keep abreast of the latest developments. [Reviewed in *Rubber Age*.]

Big Molecules. By Harry Melville. Published by Macmillan, New York. Hard cover, $5 \times 7\frac{1}{2}$ inches, 180 pages. Price: $3.95.—This delightful little book keeps the reader interested and curious from beginning to end. Starting with the general importance of macromolecules in everyday life, the author describes in clear and readily understandable terms the most important methods for the synthesis and chemical modification of typical representatives of big molecules. He proceeds then to a discussion of their molecular weight, enumerates the different methods for its determination, and explains the principles of their operation. Turning to the more practical aspects, the author devotes the last four chapters of the booklet to the presentation of the role of big molecules in the most important fields of practical application, starting with a discussion of fibers and their properties, passing on to the description of various elastomers, and finishing with the many different uses of high polymers as plastics, coatings, adhesives, insulators, and ion exchange resins.

This book makes excellent educational reading for the interested layman, but it also challenges the expert by the clarity and simplicity of its presentation. [Reviewed by H. Mark in *Journal of Polymer Science.*]

List of Publications, 1940–1959, of the British Rubber Producers' Research Association, 48–56 Tewin Road, Welwyn Garden City, Herts., England.

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RELATION BETWEEN THE ANOMALOUS FREEZING POINT DEPRESSION AND THE MECHANICAL-ELASTIC BEHAVIOR OF GELS *

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INTRODUCTION

It has long been known that potatoes and beets have a freezing point which lies under the value corresponding to the ion concentration in cell water. More recent investigations show the same phenomena in living muscle tissue of rabbits[1]. The studies carried out by Kuhn and Majer[2,3] on models from polyacrylic acid and polyvinyl alcohol show that it is not a matter specific to living cells. They show that freezing point depressions similar to those observed with natural muscle can be observed with these synthetic systems.

As is already shown in foregoing studies[4], the anomalous freezing point depression of such gels comes about in such a way that the macromolecules present as gel formers in this system form a spatial network in whose interstices only microcrystals can be formed corresponding to the small interspaces (mesh). At known widths of mesh, the freezing point depression can be calculated or, in reverse, when the freezing point depression is measured, the width of mesh is determined. We possess therefore a new method for obtaining dimensions of macromolecules in natural and synthetic materials.

Also macromolecular networks which contain other swelling agents than water show this freezing point depression. In the present work, studies of rubber swelled in benzene are described and explained quantitatively. Rubber is interesting because its width of mesh can be varied by different degrees of vulcanization.

RELATION BETWEEN E–MODULUS E_q, SWELLING DEGREE q AND WIDTH OF MESH h_q OF A SWOLLEN GEL

The swelling degree q and the elasticity modulus E_q give us some information about the structure and width of mesh of a spatial network formed by macromolecular chains as they are present in gels. On the basis of statistical considerations about the probable form of chain molecules as they were first employed for macromolecules in solution, Kuhn and coworkers[5] found for the elasticity modulus of a swollen network (gel) the relationship:

$$E_q = 3kTG' q^{\frac{1}{3}} \tag{1}$$

G' is the number of linear lattice filaments per cm³, each lattice filament being terminated at two crosslinking points. The swelling degree q is equal to the volume of a given amount of gel divided by the dry volume of the gel formers contained therein. k is the Boltzman constant, T the absolute temperature.

If the densities of the dried material and the solvent are approximately the same, we obtain the following relationship between the swelling degree q, the number G' of the lattice filaments per cm³, the dry content m per cm³ of gel and the molecular weight M_f between crosslinks when N_L is the Loschmidt number per mole:

$$\frac{M_f G'}{N_L} = m = \frac{1}{q} \tag{2}$$

the following is obtained from it:

$$M_f = \frac{N_L}{q \cdot G'} \tag{2a}$$

Equation (1) placed in Equation (2a) gives the following relationship between the molecular weight M_f between crosslinks, the E-modulus E_q and the swelling degree q of the swollen gel:

$$M_f = \frac{3RT}{E_q \cdot q^{\frac{1}{3}}} \tag{3}$$

To find the width of mesh present in swelled gels, we first examine the network in a solvent free state and ask for the average distance between the two crosslinking points, i.e., for the average distance between both ends of a lattice filament. The crosslinking in a solvent free state (e.g., the vulcanization of rubber), is imagined to be produced in such a way that two points of the macromolecules, which are accidentally adjacent, are connected whereby the molecule retains its statistical configuration. We can regard therefore each lattice filament as a statistically coiled chain molecule and ask for the average distance between the chain end points, in this case, the crosslinking points. As was shown in Reference 6, the following equation stands for the average square of the distance between the chain-end points in solvent free networks:

$$\overline{h^2} = N_m \cdot A_m{}^2 \tag{4}$$

whereby N_m is the number of statistical chain elements in the lattice filament and A_m is their length. If M_g is designated as the molecular weight of the basic molecule and s_m as the number of basic molecules in a statistical chain element, $s_m \cdot M_g$ is the molecular weight of the statistical chain element and the molecular weight between crosslinks is

$$M_f = N_m \cdot s_m \cdot M_g \tag{5}$$

If the length of the basic molecule is b, then the following is true:

$$s_m = \frac{A_m}{b} \tag{6}$$

Equations (6) and (5) inserted in Equation (4) yields:

$$\overline{h^2} = \frac{M_f \cdot A_m \cdot b}{M_g} \tag{4a}$$

As was shown at the beginning of this section (Equation (3)), the molecular weight between crosslinks M_f can be determined by measuring the swelling

degree and the elastic modulus E_q of the swollen network. By inserting Equation (3) into Equation (4a), the following equation is obtained for the average square of the length of the lattice filament in unswollen networks:

$$\overline{h^2} = \frac{3\,RT}{E_q \cdot q^{\frac{1}{3}}} \frac{A_m \cdot b}{M_s} \tag{4b}$$

Upon swelling the network in a solvent, the volume increases by a factor q, the linear dimensions consequently by the factor $q^{\frac{1}{3}}$, and the average distance square by the factor $q^{\frac{2}{3}}$. Therefore the following is obtained for the average distance squared between two crosslinked points in a swollen network:

$$\overline{h_q^2} = \frac{3\,RT\,A_m \cdot b}{M_s} \frac{q^{\frac{1}{3}}}{E_q} \tag{7}$$

DEPENDENCE OF FREEZING POINT ON THE CRYSTAL SIZE

That a microcrystal has a higher vapor pressure than a macrocrystal and that the microcrystal consequently has a lower melting point is shown by putting the reversible work which is needed to vaporize a given amount of a macrocrystal and to condense it onto a microcrystal, equal to the increase of the interface energy of the microcrystal toward the surrounding liquid. This fact, known long ago, was used for the first time by Kuhn for the explanation of observations mentioned in the introduction[8]. The following equation results from Reference 8 for the freezing point depression of a cubic microcrystal of edge length a in contrast with a macrocrystal:

$$\delta T_a = -\frac{4 \cdot 10^3 \cdot E_m \, \sigma_{\text{cryst., liq.}}}{\rho_{\text{cryst.}} \cdot RT_0 \, a} \tag{8}$$

where E_m is the molecular freezing point depression, $\rho_{\text{cryst.}}$ is the density of the crystal, R is the gas constant, T_0 is the normal melting temperature and $\sigma_{\text{cryst., liq.}}$ is the interfacial tension between the crystal and its melt.

The interfacial tension between a benzene crystal and liquid benzene is estimated at about $\sigma_{\text{cryst., liq.}} = 4$ erg cm^{-2} by the order of magnitude from the surface tension of liquid benzene and the density difference between solid and liquid benzene since up to now no exact value has been determined. Studies for the measurement of σ are in process. Values calculated by A. V. S. de Reuck on the basis of theoretical considerations were published recently for the interfacial tension of ice-water (Nature (London) **179**, 1119 (1957)).

FREEZING POINT OF GELS

Now we will assume that the magnitude of the benzene crystal, which is formed on cooling, is limited by the network of molecular chains. The network segments are coiled statistically and are subject to Brownian movement even in crosslinked gels so that they can give way to a certain extent to a growing crystal. The points of crosslinkage which belong to four network segments each simultaneously possess however only limited mobility. We therefore regard the root mean square distance between end points of a lattice filament as the upper limitation of the crystal size possible in the gel:

$$a \simeq \sqrt{\overline{h^2}_q} \tag{9}$$

A relationship between the freezing point depression δT referred to pure benzene, the swelling degree q and the elastic modulus E_q of swollen rubber is obtained from Equations (7) and (8):

$$\delta T = -\frac{4\,\sigma_{\text{cryst., liq.}}\,10^3\,E_m}{\rho_{\text{cryst.}}\,RT_0}\left(\frac{M}{3\,RT_E\,A_m b}\right)^{\frac{1}{2}}\frac{E_q^{1/2}}{q^{1/6}} \tag{10}$$

T_E is the temperature at which the elasticity of the swollen gel was measured. The lengths of the statistical chain element A_m and the basic molecule b are tabulated[9] and the remaining constants except σ, which has already been spoken spoken of, can be found in handbooks. Therefore the following equation can be written:

$$\delta T = -K\frac{E_q^{1/2}}{q^{1/6}} \tag{10a}$$

TABLE I

SUMMARY OF RESULTS WITH RUBBER

Designation of sample Property		A	B	C	D
Elastic modulus	E_q	$4.00 \cdot 10^6$	$10.16 \cdot 10^6$	$18.45 \cdot 10^6$	$26.5 \cdot 10^6$
Degree of swelling	q	4.65	4.01	3.07	2.58
Freezing point depression calculated	$\delta T_{\text{calcd.}}$	7.3	10.7	16.8	20.8
Freezing point depression measured	δT_{found}	6.4	11.0	17.0	20.9
Vulcanization points per cm³ of gel	μ	$5.94 \cdot 10^{18}$	$16.6 \cdot 10^{18}$	$25.3 \cdot 10^{18}$	$58.1 \cdot 10^{18}$
Average distance between vulcanization points	a'	$5.52 \cdot 10^{-7}$	$3.92 \cdot 10^{-7}$	$3.40 \cdot 10^{-7}$	$2.58 \cdot 10^{-7}$
Average length between crosslink ends	a	$17.0 \cdot 10^{-7}$	$10.5 \cdot 10^{-7}$	$7.45 \cdot 10^{-7}$	$5.99 \cdot 10^{-7}$
Ratio of $a:a'$	$\dfrac{a}{a'}$	3.08	2.68	2.19	2.32

EXPERIMENTAL

Four sheets of pure rubber whose degree of vulcanization was varied by application of different amounts of sulfur were studied. These were prepared by the Longstroff firm (Aarau) especially for the experiments. The sheets were swollen to saturation in pure benzene. The swelling equilibrium is reached after approximately 30 hours. The q-values then obtained are shown in Table 1, Line 2.

In order to obtain the elastic modulus of the swollen gel samples, a circular disc of the gel was compressed using different loads by a piston moving practically free of friction, its positions being observed by means of a cathetometer. The results are indicated in the first horizontal of Table 1.

To study the freezing behavior, a piece of gel was placed in a well isolated reagent glass is a constant cooling bath of $-70°$ C; the temperature in the gel was measured with a thermoelement one junction of which was placed in the gel, and registered photographically with a sensitive galvanometer (see Reference 10).

RESULTS

The cooling curves observed with samples of the four types of rubber, swollen in benzene to saturation are produced in Figure 1. A particularly clear picture is obtained when calculating from the course of the cooling curves the relative amount ϑ of benzene having passed from the liquid to the crystallized state in the different temperature regions. In Figure 2, $\frac{d\vartheta}{dt}$ is shown as a function of temperature t, that is, the relative amount of benzene present passing into the crystalline state in a temperature interval $dt = 1$. An approximate formula for the calculation of the relative amount of crystalline benzene present in each increment is explained and derived in Reference 2. Since according to Equa-
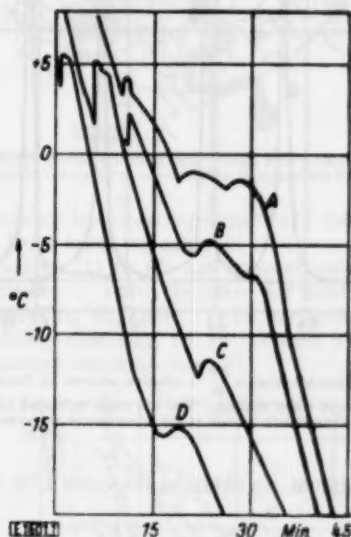
Fig. 1.—Freezing curves for swelled rubber samples of different degrees of vulcanization. A is vulcanized the least and D the most.

tion (8) each temperature $T = T_0 - \delta T_a$ corresponds to the formation of crystals of a well determined linear dimension a, the curves of Figure 2 give directly the crystal magnitude spectra.

For the numerical evaluation of Relationship (8) we bear in mind that for benzene $E_m = 5.12$ degrees gmole^{-1}, $\rho_{cryst.} = 1.01$ g cm^{-3}, $T_0 = 278.5°$ K and that $\sigma_{cryst., liq.}$ can be estimated at approximately 4 erg cm^{-2} while $R = 8.3 \cdot 10^7$ erg degree^{-1} mole^{-1}. Using these values in the evaluation of Equation (8) we have:

$$\delta T_a = - \frac{4 \cdot 10^3 \cdot 5.12 \cdot 4}{1.01 \cdot 8.3 \cdot 10^7 \cdot 278.5} \frac{\xi}{a} = - 3.5 \cdot 10^{-6} \frac{\xi}{a} \qquad (8a)$$

whereby factor ξ on the right side of this equation accounts for the existing uncertainty in the estimation of $\sigma_{cryst., liq.}$ as well as the effect of the deviation of the crystal form from the form of a cube. ξ is therefore a dimensionless numeri-

cal factor which presumably does not deviate much from 1. The linear dimensions a of the benzene crystals corresponding to the different ranges of δT_a are indicated by a scale parallel to the abscissa in Figures 2 and 4.

Table 1 gives some data concerning the four rubber samples whose freezing curves were represented in Figure 1. When we calculate the freezing point depression δT from E_q and q with the help of Formula (10a) and thereby choose K so that the sum of the quadratic deviations of the measured δT_a values from the
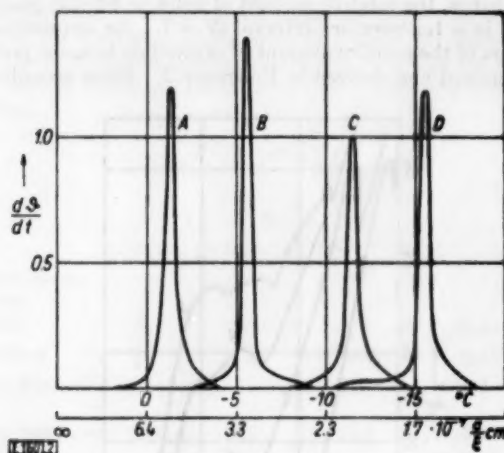
Fig. 2.—Crystal magnitude spectra, that is $\frac{d\vartheta}{dt}$ = relative amount of benzene crystallizing within a temperature interval of one degree when cooling. The a/ξ scale indicated below the temperature scale gives the approximate length of the crystals formed at the temperature concerned [ξ being for good reasons not much different from unity].

calculated ones is a minimum, we obtained the value $4.73 \cdot 10^{-3}$ for the constant K and therewith

$$\delta T = - \, 4.73 \cdot 10^{-3} \, \frac{E_q^{1/2}}{q^{1/6}} \tag{10b}$$

The relatively slight deviation of the observed δT value from the δT calculated with this empirical K value and Equation (10a) shows that the theoretical formula (10a) is indeed a satisfactory representation of the connection between freezing point, swelling degree and elastic modulus of the gel samples.

By inserting in Equation (10) the parameters valid or estimated for rubber and benzene it is possible to interpret the value often used for the constant K to a certain degree theoretically. Introducing the numerical values already mentioned for the parameters E, $\rho_{cryst.}$ T_E, R, and $\sigma_{cryst.,liq.}$

$$Mg = 68$$
$$T_E = 278 \text{ degree}$$
$$A_m = 13.10^{-3} \text{ cm}$$
$$b = 5.0 \cdot 10^{-3} \text{ cm,}$$

we get $K' = 1.33 \cdot 10^{-3}$.

Fig. 3.—Within a sphere around a vulcanization point with a radius A_e, 10–27 crosslinking points belonging to other lattice filaments are found.

K' is 3.5 times smaller than the experimentally found K. The deviation can be traced to the three following reasons:

First, the relationships (1) to (8) are approximations for dilute systems. They are not quantitatively valid therefore for relatively small degrees of swelling as found according to Table 1. In particular, the approximations relate to pure probability elasticity, i.e. to the case where the stretched and unstretched phases possess the same energy[11].
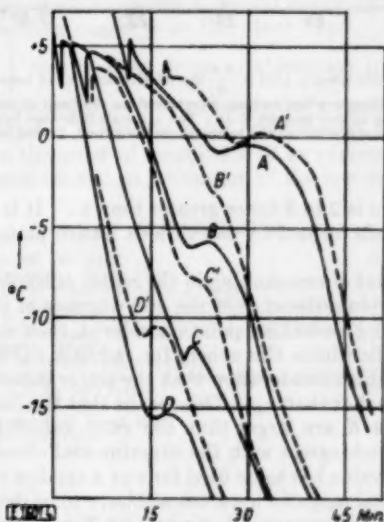
Fig. 4.—Cooling curves after the first (continuous curves) and the second (broken curves) freezing of swollen rubber samples.

Second, the value of the interfacial tension $\sigma_{cryst., liq.} = 4$ erg cm^{-2} is an order of magnitude estimation.

A third possible correction factor depends on an arbitrary assumption involved in Statement (9) $a \simeq \sqrt{\overline{h_q{}^2}}$. The number μ of the vulcanization points per cm^3 of gel amounts to $\dfrac{G'}{2}$, because each lattice filament ends in two vulcanization points and because four lattice filaments are issuing from each vulcanization point (Table 1, Line 5). If we distribute these vulcanization points in the gel in a rocksalt lattice-like manner the distance between two adjacent vulcanization points is equal to a' (Table 1, Line 6). If we compare a with a'
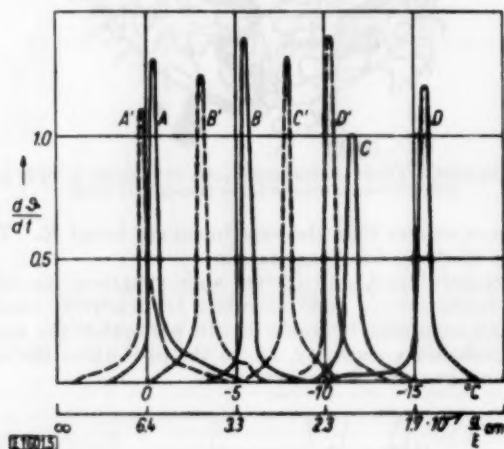
FIG. 5.—Crystal magnitude spectra, that is, $\dfrac{d\vartheta}{dt}$ the relative amount of benzene crystallizing within a temperature interval of one degree when cooling, ascertained on the basis of the first and second cooling curves given in Fig. 4 for the rubber samples A-D. The a/ξ scale indicated below the temperature scale gives the approximate length of crystals at the temperature concerned, ξ being for good reasons not much different from unity.

(Line 8), we see that a is 2 to 3 times greater than a'. It is apparent therefore that the statistical coils formed by the various lattice filaments are interpenetrating.

If we place one point of crosslinking in the center of a sphere whose radius h_q corresponds to the average distance of the end distance of the four lattice filaments issuing from the crosslinking point considered, then some 10 to 27 foreign vulcanization points lie within this sphere (or radius h_q) (Figure 3). It is possible on the basis of this consideration that the linear dimension of the crystal possible in a gel is smaller than h_q. This means that the freezing point depression and the constant K are larger than the value calculated from Equation (10), a prediction which agrees with the experimental observation.

Whether another value has to be used for σ or a smaller value than h_q has to be chosen for the crystal magnitude values will have to be determined by further studies, for example by measurement of σ and by X-ray investigation of frozen gels.

FREEZING DAMAGE

The microcrystals exert a force on the surrounding polymer chains. This force can increase up to the breaking strength of the chains. Thus, freezing damage in the network has often been ascertained in living tissue[1] and can be related quantitatively to the breaking of individual network segements in aqueous gels[5]. Such freezing damage occurs with rubber in benzene.

The continuous curves of figures 4 and 5 show the temperature as a function of time and the crystal magnitude spectra occurring upon freezing the first time for the four samples of swollen rubber while the broken lines represent the corresponding quantities of the same samples when freezing the second time. After the first and before the second freezing, these samples were thawed and brought to equilibrium with pure benzene. The degree of swelling is practically not changed by the freezing while the elastic modulus and the freezing point depression decrease in such a way that the relationship (10a) is essentially valid not only for the first but also for the second freezing.

SUMMARY

The elastic modulus and degree of swelling of rubber samples differing in the degree of vulcanization and swollen in benzene are determined as well as the anomalous freezing point depression. The anomalous freezing point depression obtained by observing the cooling curve amounts to about $20°$ C for highly vulcanized samples. The anomalous freezing point depression δT_a is ascribed to the restrictions, which are conditioned by the gel structure, of the length a of the crystals forming in the interior of the gels, as has been done with aqueous gels in a similar manner. On the basis of the statistical-thermodynamic theory of rubber elasticity quantitative relationships are shown to exist between the width of mesh of the spatial network obtained in the swollen sample, i.e. between the magnitude of the crystals possible in the gel on one hand and the E-modulus E_q of the gel at swelling degree q on the other hand. A theoretical relation

$$\delta T = \left[- K \frac{E_q^{1/2}}{q^{1/6}} \right]$$ results from these relationships in conjunction with a

thermodynamic relationship between the crystal magnitude and the melting point. This relationship is confirmed by experimental results. The value of constant K is within the order of magnitude to be expected on the basis of the theoretical considerations and an estimation of the interfacial tension $\sigma_{cryst., liq.}$.

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STRESS-STRAIN ISOTHERM FOR
POLYMER NETWORKS *

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INTRODUCTION

The elastic free energy of a polymer network may be expressed, according to the molecular theory of rubber elasticity, as follows:

$$\Delta F_{el} = kT\nu[Tr(\lambda^T\lambda - \mathbf{E}) + (2/f)\ln(V/V^0)] \tag{1}$$

where λ is the deformation gradient, expressed in matrix form, with elements $\lambda_{ij} = \partial x_i'/\partial x_j$, x_j, and x_i' being Cartesian coordinates of a representative point before and after deformation, respectively; λ^T is the transpose of λ; $\mathbf{E}$ is the identity matrix of order three; ν is the number of effective chains in the network; f is the functionality of the network junction ($f = 4$ for the usual case of a crosslinked network); V is the volume of the sample; and V^0 is its volume in the reference state for which the trace of $(\lambda^T\lambda - \mathbf{E})$ vanishes. The choice of (isotropic) reference state is rendered unique by stipulating that the summation $\sum_t[(\langle r_t^2\rangle/\langle r_t^2\rangle_0) - 1]$ over all network chains shall vanish therein; $\langle r_t^2\rangle$ is the mean-square end-to-end distance of chain t when the network is in the specified state and $\langle r_t^2\rangle_0$ is its value for the free chain[1,2]. Gaussian chains are assumed; for real networks, deviations from the gaussian representation of the chain end-to-end distribution become significant only at higher elongations than are of concern here.

The second term in Equation (1) arises from consideration of the entropy of the spatial distribution of the network junctions. For deformations at constant volume V, such as are exclusively treated here, this term is constant and hence may be disregarded. Furthermore, if by suitable choice of coordinate axes, λ is rendered diagonal, Equation (1) may then be recast for present purposes as follows[1,2]:

$$\Delta F_{el} = kT\nu[\langle\alpha\rangle^2(\lambda_x^2 + \lambda_y^2 + \lambda_z^2) - 3] \tag{2}$$

where $\lambda_x, \lambda_y, \lambda_z$ are the principal extension ratios relative to the isotropic state of volume V, and $\langle\alpha\rangle$ is the linear dilation factor[2] defined by $\langle\alpha\rangle^3 = V/V^0$. For simple elongation (at constant volume), let $\lambda_x = \alpha$ and $\lambda_y = \lambda_z = \alpha^{-\frac{1}{2}}$. The stress referred to the initial cross section is given by the well-known relation which follows at once from Equation (2)

$$\tau = kT(\nu/V)\langle\alpha\rangle^2(\alpha - 1/\alpha^2) \tag{3}$$

If the network contains a fixed quantity of a diluent such that the volume fraction of polymer is v_2, then the stress referred as before to the unswollen,

unstrained cross section becomes[2,3]

$$\tau = kTv_2^{-\frac{1}{3}}(v/V)\langle\alpha\rangle^2(\alpha - 1/\alpha_i) \tag{3'}$$

V veing the unswollen volume, and α the extension relative to the swollen rest state. The notation here employed differs slightly from that used in Reference 2; our $\langle\alpha\rangle$ and V correspond to the $\langle\alpha\rangle_0$ and V_0 of that reference. With V thus defined, the quantity $(v/V)\langle\alpha\rangle^2$ should be invariant to dilution[2].

Alleged deviations from this equation of state of the molecular theory have elicited the suggestion that terms should be appended to Equation (1) which contain the second strain invariant $Tr((\lambda^{-1})^T\lambda^{-1})$. Thus, from purely phenomenological considerations equations of more general form have been advocated to replace Equation (2)[4–6]. The simplest of these is the following[6]:

$$\Delta F_{el} = C_1(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) + C_2(\lambda_x^{-2} + \lambda_y^{-2} + \lambda_z^{-2} - 3) \tag{4}$$

where C_1 and C_2 are parameters of a nature unspecified. The corresponding relation for the stress in simple elongation becomes

$$\tau = 2C_1(\alpha - 1/\alpha^2) + 2C_2(1 - 1/\alpha^3) \tag{5}$$

Correspondence of $2C_1$ with $kT(v/V)\langle\alpha\rangle^2$ of Equation (3) is apparent. Values of $2C_1$ obtained by application of Equation (5) to experimental data should not however be unreservedly identified with the latter quantity, inasmuch as the C_2 term finds no basis in molecular theory. Hence, it would not be justified to assume that whatever perturbation is responsible for the second term has no effect on the value of the first.

The present experimental investigation was undertaken for the purpose of ascertaining the dependence of C_2 on the constitution and chemical nature of the polymer system, and on the experimental conditions adopted for determining the stress–strain relationship. Five different polymer types have been investigated. The influence of temperature, dilution, degree and method of crosslinking, and period of relaxation at each elongation have been explored. The results afford compelling evidence for the conclusion that the C_2 term is baseless.

EXPERIMENTAL

Materials.—Characterization of the materials used in this investigation is summarized in Table I. Crosslinking was accomplished by the methods indicated, and as further described below.

Natural rubber samples NR-1 to NR-4 were prepared from latex films about 1 mm in thickness supplied by Roberts and Mandelkern[7] whose assistance is gratefully acknowledged. The samples were sealed in vacuum and placed within a cylindrical Co^{60} source giving a uniform γ-ray dose rate of 0.610 rad/hr. Crosslinking was performed at room temperature; the dosages are given in the last column of Table I.

Sample NR-7 was prepared by similarly crosslinking a sheet comprising a solution of pale crepe rubber and n-hexadecane, the volume fraction of the former being 0.40. Irradiation was performed in an atmosphere of pure nitrogen as previously described. For certain of the dynamometric experiments, the diluent was subsequently removed in part by evaporation in vacuum

at *ca.* 50° C; in others, total removal was accomplished by extraction with benzene, followed by removal of residual benzene in vacuum at 50° C.

Sample NR-6 is a representative sulfur vulcanizate (see reference *a* of Table I), made available to us through the courtesy of the National Bureau of Standards.

The silicone polymer, a linear poly-(dimethylsiloxane) of high molecular weight ($\bar{M}_w \cong 650{,}000$) was supplied by the Silicone Fellowship of the Dow-Corning Corporation at Mellon Institute. Residual catalyst was removed by washing with dilute aqueous acid in accordance with the detailed procedure described by Osthoff, Bueche, and Grubb[3]. Vulcanization with benzoyl per-

TABLE I

CHARACTERISTICS OF SAMPLES

Sample designation	Material	Crosslinking
NR-1	Natural rubber	γ rad, 14.4×10^6 R
NR-2	Natural rubber	γ rad, 28.8×10^6 R
NR-3	Natural rubber	γ rad, 43.2×10^6 R
NR-4	Natural rubber	γ rad, 39.0×10^6 R
NR-6	Natural rubber	Sulfur-accelerator vulcanized[a]
NR-7	Same with 60% by vol. *n*-hexadecane	γ rad, 27.7×10^6 R
S-1	Poly-(dimethylsiloxane)	Benzoyl peroxide, 1.65%[b]
S-2	Poly-(dimethylsiloxane)	γ rad, 14.8×10^6 R
S-3	Same with 51% by vol. *n*-hexadecane	γ rad, 27.7×10^6 R
B-1	Butyl rubber	Sulfur-accelerator vulcanized[c]
B-2	Butyl rubber	Sulfur-accelerator vulcanized[c]
PMMA	Poly-(methyl methacrylate)	Copolymer of MMA with 0.044% of ethylene dimethacrylate
PEA	Poly-(ethyl acrylate)	Copolymer of EA with 0.097% of ethylene dimethacrylate

[a] Ingredients by weight: 100 rubber, 5.0 ZnO, 2.5 *S*, 1.0 mercaptobenzothiazole, 0.5 phenyl 2-naphthylamine; one hour at 110° C.

[b] Heated 20 min at 120° C, 60 min at 160° C.

[c] Ingredients by weight: 100 Butyl rubber (*Y*-110), 1.0 ZnO, 1.5 *S*, 1.0 stearic acid, 0.75 Butyl zimate; 2 hr. at 140° C. Sample B-2 was obtained by extraction of antioxidant from B-1; concurrently, degree of crosslinking was diminished somewhat.

oxide was accomplished by press molding a film from polymer containing the desired percentage of the peroxide, and heating as indicated in Table I. Sample S-2 was crosslinked by γ radiation according to the procedure described above. Sample S-3 was prepared by pressing a film from a mixture of the indicated composition. The film was protected from distortion prior to creation of a continuous network structure through radiation crosslinking by mounting it within a rectangular frame. Irradiation was performed under purified nitrogen.

Butyl rubber, an isobutylene polymer modified by copolymerization with *ca.* 2% of isoprene units, was vulcanized with sulfur and an appropriate accelerator (see footnote to Table I).

Suitably crosslinked polymers of methyl methacrylate and of ethyl acrylate were made available to us through the courtesy of Dr. J. C. H. Hwa of the Research Department of the Rohm and Haas Company.   These polymers were prepared by copolymerizing the respective monomers with the percentages of ethylene dimethacrylate indicated in Table I.   Approximately 0.05% by weight of azo-bis-isobutyronitrile was used as initiator, the polymerizations being conducted in a mold to yield sheets of appropriate thickness (1 mm). The former monomer was polymerized for 21 hr at 65° C followed by an hour at 125° C; the latter was polymerized 20 hr at 50° C, and three hours at 125° C.

Except for those samples prepared by crosslinking in the presence of a diluent, none of the crosslinked materials contained soluble components exceeding 5% of the total by weight.   Such soluble components as were present were removed by extraction with solvents prior to performance of measurements. In order to minimize the oxidative deterioration of the natural rubber and butyl rubber (polyisobutylene) samples, approximately 0.5% of phenyl 2-naphthylamine was incorporated after extraction.

Samples for investigating the effects of diluents on the stress–strain relationship were prepared by swelling the previously crosslinked sample in the appropriate diluent until the desired quantity was absorbed.   The swollen sample was allowed to stand for at least 2 hr before use in order to assure uniform distribution of the diluent.   The quantities incorporated were readily determined by weighing.   In this manner, samples of natural rubber, butyl rubber, and the silicone polymer were diluted with n-hexadecane subsequent to crosslinking of the polymer.   The PMMA [poly-(methyl methacrylate)] was similarly diluted with diethyl phthalate.   The silicone sample S-1 was diluted in one instance with a low molecular weight dimethylsiloxane polymer, Dow-Corning 200 (D-C-200) fluid, having a degree of polymerization ca. 40.

Samples approximately 1 mm wide by 40 mm in length were cut from the crosslinked polymer sheets using a die consisting of a pair of razor blades mounted parallel to each other and separated by a distance of 1 mm.   In a few instances a greater sample width was chosen in order to increase the tension in the interests of greater accuracy.   Cross sections of samples were measured with the microscope.   The method permitted an accuracy within ±0.010 mm for individual measurements.   Cross sections were measured at intervals of 5 mm along the sample, the average value being used for converting the measured tension to the stress τ referred to the initial cross section.   Samples whose cross sections varied by more than 4% were discarded.

Dynamometry.—The dynamometer was similar in design and operation to that described previously[9].   The elongation of the sample was not, however, varied continuously as in the reference cited.   Instead, the length was fixed and the tension was recorded continuously over an interval of time; or the force was merely taken at the conclusion of a specified interval as described more fully below.

Each end of the sample was clamped between a pair of small metal plates held together by screws.   The lower clamp was attached to the lower end of a vertically mounted brass bar, the upper end of which carried the strain gauge assembly.   The latter consisted of a rack and pinion permitting manual adjustment of the vertical position of the strain gauge.   The upper clamp was suspended from the strain gauge by a nickel rod.   The sample, the clamps and lower portion of the brass bar were placed within the sample chamber consisting of a 3-cm glass tube closed at its lower end.   The sample chamber was im-

mersed in a liquid thermostat controlled to $\pm 0.1°$ C. The strain gauge was protected against the effects of temperature by circulating water through the metal plate on which it was mounted.

The length L of the sample, taken as the distance between clamps, was measured with a cathetometer. Adjustment of the vertical position of the strain gauge, to which the upper clamp was attached, permitted the length to be varied as desired. The length L_0 of the sample in the rest state usually was *ca.* 3.0 cm.

The sample chamber was charged with an inert atmosphere—usually nitrogen of high purity—and a slow stream of the inert gas was passed through the chamber throughout each experiment. A minimum current of gas was employed in those experiments in which the sample contained a diluent, in order
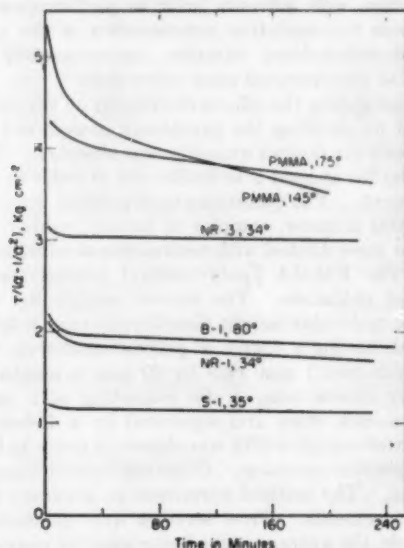
FIG. 1.—Reduced stress plotted against time at constant elongation $\alpha = 1.50$ in all cases.

to minimize possible loss thereof. At the conclusion of such experiments the weight of the sample was compared with its original value in order to assure that the composition had not undergone appreciable change during the course of the experiment.

Measured tensions were generally in the range of 10 to 200 g. The capacity of the strain gauge was 670 g; its linear response was 0.042 mv/g under an emf of 10 v. The output of the strain gauge was delivered to a Speedomax Recorder (Leeds and Northrup); the emf for full scale deflection could be varied from 1 to 5 mv. A preamplifier was employed in a few of the experiments where an increase in sensitivity was desired.

The strain gauge was calibrated directly by using known weights. The calibration did not vary preceptibly over long periods of time, provided however that the voltage applied to the strain gauge was accurately maintained at a constant value, and that spurious drifts in the zero point were duly corrected.

Accordingly, the voltage was determined and adjusted to the standard value at frequent intervals. The zero point was ascertained before each recorded determination of the value of the stress. It was necessary therefore to check the zero point at frequent intervals during a given experiment without introducing undesired alterations in the elongation of the sample. This was accomplished by temporarily securing the position of the nickel rod which supported the upper clamp and then disconnecting the strain gauge. After the zero point had been redetermined, the gauge and rod were reconnected and the measurements resumed.

The strain gauge and recorder system were so operated as to assure an accuracy of at least 99–98% in the measured tensions. The tensions were converted to stresses τ, referred to the initial (rest) cross section, through division by the value of the cross-sectional area determined as described above. Un-
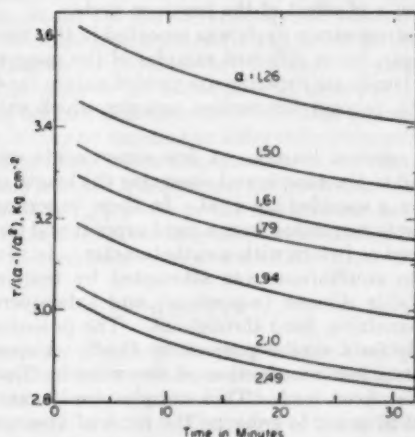
Fig. 2.—Reduced stress for NR-6 at 35° C plotted against time for the various elongations indicated.

certainty in the mean cross section (*ca.* $\pm 2\%$) generally exceeded the percentage error in the tension. The absolute uncertainties in the stresses therefore are greater than the relative errors for a series of stress determinations conducted on the same sample.

Tensions were readily measured and recorded continuously as a function of time at fixed length using the apparatus described. Typical time plots are shown in Figures 1 and 2.

Except where indicated otherwise, stress-strain curves were obtained according to the following *standard procedure*. The sample was extended by successive increments, the tension being observed after an interval of 3 min at each length. Elongation increments of about 5% were usually chosen in the range from 0 to 25% ($\alpha = 1.00$ to 1.25). Intervals of about 10% were then chosen for greater elongations. In general, the range was confined to a maximum elongation of about 100%; measurements at higher elongations were rendered impractical either by likelihood of rupture of the sample or by possible incidence of crystallization. After reaching the maximum elongation, the

tension was determined for successively decreasing lengths following a similar schedule.   The degree of hysteresis was manifested in the divergence between ascending and descending phases of the strain cycle.   This divergence (i.e., size of the hysteresis loop) depends of course on the time interval at each step. The foregoing standard procedure, employing an interval of 3 min and a maximum elongation of about 100%, was adopted in order to provide a satisfactory basis for comparing results for different samples.

The rest length L_0 was established within an accuracy of *ca.* ±0.5% by extrapolating the initial tension-length measurements for the extension phase of the cycle to a tension of zero.   The rest length observed immediately at the conclusion of a stress-strain cycle exceeded L_0 slightly, the deviation depending on the magnitude of the hysteresis for the polymer concerned.   However, after standing for a period of 10 to 50 hr, the original value (L_0) was re-established. Repetition of the experiment thereafter reproduced the previous stress-strain loop, without evidence of effect of the previous cycle.

In general, the stress-strain cycle was repeated in this manner at least three times on each sample, or on different samples of the same polymer under the same conditions.   Duplicate experiments yielded values for C_2 which generally agreed within ±5% (except for swollen samples which exhibited very small values for C_2).

Experiments at constant tension.—A few experiments were carried out by applying a fixed load to the sample and observing the length either as a function of the time or after a specified interval.   In these experiments a weight was attached to the sample suspended from a rigid support and the distance between clamps was measured as before with a cathetometer.   In several instances improved approach to equilibrium was attempted by temporarily swelling the sample with a volatile diluent (n-pentane) and subsequently removing the diluent, the load remaining fixed throughout.   The procedure resembled that employed previously for a similar purpose by Gee[10].   A special apparatus was designed which permitted introduction of the volatile diluent to the sample while supporting the fixed load.   Thin samples (*ca.* 2 mm × 0.5 mm) were generally employed in order to enhance the rates of absorption and of subsequent removal of the diluent.   Approximately 10 min sufficed for the sample to swell three- to fourfold in volume.   After a further 10 min, the diluent was removed under vacuum, approximately 2 hr being required for this purpose.

Swelling equilibrium.—The degree of swelling at equilibrium with excess diluent was measured for several polymers in order to secure an independent determination of the degree of crosslinking.   Two standard methods yielding results in close agreement (within 1%) were used.   One of these consisted in weighing the sample before and after swelling equilibrium was established, which required from $\frac{1}{2}$ to 2 hr.   The second method involved determination of the linear dimensions using a measuring microscope.   The former method was preferred.   Even in the case of natural rubber, the degree of swelling remained constant for periods as great as 24 hr.

The results of swelling determinations are given in Table II.   Densities given in the third column were used for deducing the volume concentration (column four) from the weights measured according to the first method.   The elasticity parameters $\langle \alpha \rangle^2 (v/V)$ were calculated for two of the polymers using the swelling equilibrium equation[2,3]

$$(v/V)\langle \alpha \rangle^2 (v_2^{\frac{1}{3}} - v_2/2\langle \alpha \rangle^2) = - (N_a/V_1)[\ln(1 - v_2) + v_2 + \chi_1 v_2^2] \qquad (6)$$

TABLE II

EQUILIBRIUM SWELLING RESULTS AT 25° C

Sample	Swelling liquid	Polymer density 25° C	Vol from polymer at equil, v_2	$\langle \alpha \rangle^2 (v/V)$ moles $cc^{-1} \times 10^9$	$2 C_1$ calc kg cm^{-2}
NR-1	Benzene	0.91	0.119	4.5[a]	1.17 (30° C)
NR-3	Benzene	0.91	0.173	10.4[a]	2.67 (30° C)
NR-6	Benzene	0.91	0.183	11.9[a]	3.05 (30° C)
S-1	Benzene	0.97	0.170		
B-1	Cyclohexane	0.93	0.160	6.6[b]	1.82 (49° C)
B-2	Cyclohexane	0.93	0.140	5.7[b]	1.41 (39° C)
PMMA	Acetone	1.19	0.170		

[a] Calc. from Equation (6) assuming $\chi_1 = 0.42$; see Reference 11.
[b] Calc. from Equation (6) assuming $\chi_1 = 0.43$; see Reference 12.

where V_1 is the molar volume of the diluent, N_a is Avogadro's number, and χ_1 is the interaction parameter for the solvent-polymer system. The value of χ_1 for benzene-rubber as established by osmotic and vapor pressure measurements is 0.42 ± 0.01^{11}. That for cyclohexane-polyisobutylene, similarly determined, is 0.43 ± 0.01^{12}. The value of $\langle \alpha \rangle^2$ is not directly susceptible to measurement; however, considering the fact that these networks were prepared by crosslinking in the random state, it may be assumed to differ little from unity. Accordingly, $\langle \alpha \rangle^2$ may be equated to unity in the denominator of the second term in parentheses on the left-hand side of Equation (6), the contribution of this term being minor. The values of $2C_1$ calc given in the last column have been calculated from the foregoing quantities according to the relationship $2C_1$ calc $= kT(v/V)$ $\langle \alpha \rangle^2$, which may be inferred from comparison of Equations (5) and (3).

RESULTS

Critique of the procedure and the treatment of data.—The change of stress with time is illustrated in Figure 1 for various polymers held at the extension $\alpha = 1.50$. The stresses have been converted to the *reduced stress* $\tau/(\alpha - 1/\alpha^2)$, as suggested by Equations (3) and (5). The range of the ordinate scale is thereby greatly reduced and comparison of stress relaxation for the various polymers is correspondingly facilitated. Although stress relaxation is affected somewhat by the degree of crosslinking and the temperature, its variation from one polymer to another is much more striking. The manifestation of stress relaxation diminishes in the following order: poly-(methyl methacrylate) (PMMA) at 145° C, PMMA at 175° C, natural rubber (NR), butyl rubber (B), and poly-
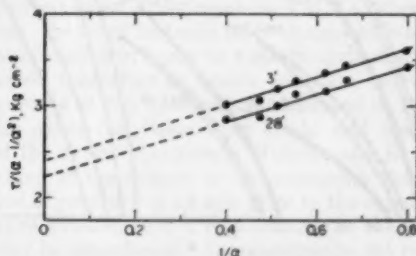
FIG. 3.—Reduced stresses taken from curves of Figure 2 at 3 min and at 28 min plotted against $1/\alpha$.

TABLE III

INFLUENCE OF TIME INTERVAL AT EACH LENGTH

Sample	° C	Time interval, min	$2 C_2$, kg cm^{-1}
NR-6	35	3[a]	1.70
NR-6	35	28[a]	1.70
NR-6	34	3	2.00
NR-3	34	3	1.60
NR-3	34	20	1.52
NR-6	59 (in air)	3	2.00
NR-6	59 (in air)	30	2.40
PMMA	145	3	4.80
PMMA	145	9	4.40
PMMA	145	30	3.60

[a] Based on measurements conducted using a different sample at each elongation; from Figure 3.

(dimethylsiloxane) (S).   This order conforms with the proximity to the glass transition temperature.

The course of relaxation of stress over the more important initial interval of time is shown in Figure 2 for different samples of the same polymer, NR-6, stretched to the various elongations indicated.   The curves are approximately parallel; i.e., the changes in reduced stress for periods up to 30 min are approximately independent of α.   Values of the reduced stress taken from the curves in Figure 2 at 3 min and at 28 min are plotted in Figure 3 against $1/\alpha$ as suggested by the Mooney equation, Equation (5).   The slopes yield the values for $2 C_2$ given at the top of Table III.   Whereas the intercept $2 C_1$ in Figure 3 diminishes with the length of the time chosen, the slope $2 C_2$ is independent thereof within experimental error.   It is to be noted that these results were obtained by employing a different sample for each elongation, this being in contrast to the stepwise procedure used in obtaining the main results presented below.
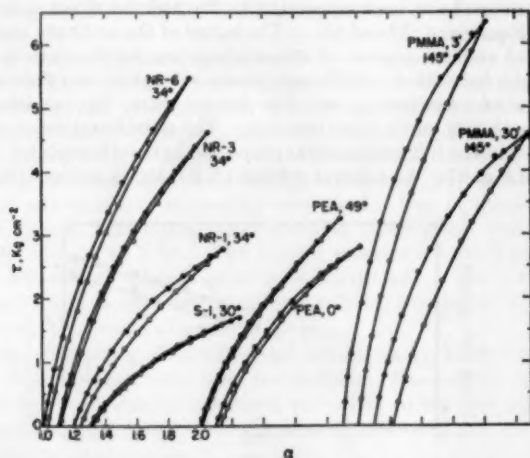
FIG. 4.—Representative stress-strain results for samples indicated.   Abscissa scales shifted by integral units of 0.1.   Points ● for elongation phase and ○ for retraction phase of the standard procedure cycle. Time interval 3 min at elongation except for PMMA as noted on graph.

In order to simplify performance of experiments, and to eliminate errors arising from individual differences between samples as well, a procedure was sought for securing the entire stress–strain curve from a single sequence of experiments performed on the same sample.   After due exploration of the variables involved, the standard procedure set forth in the experimental section finally was adopted.   Thus, a given specimen was subjected to successively increasing elongations, the tension being recorded after 3 min at each stage. Upon reaching the maximum elongation, the length was successively decreased in corresponding increments, the tension likewise being recorded after an interval of 3 min at each elongation.   Representative results are shown in Figure 4.
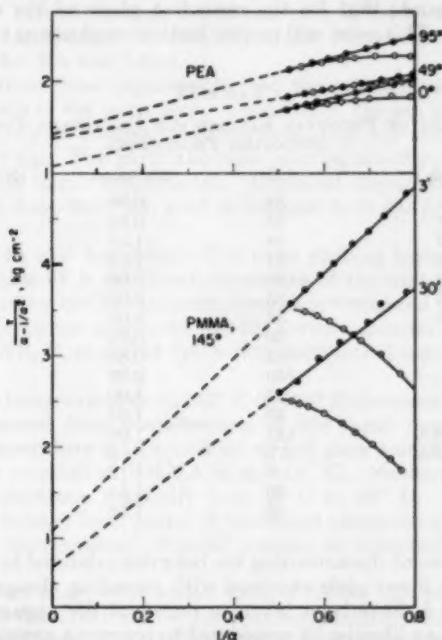
Fig. 5.—Reduced stresses plotted against $1/\alpha$.   Same data as given in Figure 4.

Included for comparison is an experiment on PMMA where the interval was increased to 30 min.   In every instance prior elongation was avoided or, if the sample had been subjected previously to a strain cycle it was allowed to stand for a sufficient period thereafter to assure complete recovery of its original length.   The magnitude of the hysteresis is indicated in Figure 4 by the disparity between the curve for diminishing strain and that obtained for the extension phase of the cycle.   Gumbrell, Mullins, and Rivlin[13] reported that preliminary stretching of the sample to the maximum elongation for 15 min, followed by a period of recovery of 15 min prior to the experiment, reduced the hysteresis.   We have avoided such a step because of the uncertain influences which might thereby be introduced.   In experiments not reported here it was found, however, that the value of C_2 was substantially unaffected by introducing a stretching cycle immediately prior to the experiment.

The representative results shown in Figure 4 are presented also in Figure 5 where the reduced stress is plotted against $1/\alpha$ for $\alpha > 1.25$; experimental error is excessive for smaller α.   The points for the extension phase of the cycle fall approximately on a straight line in accordance with the Mooney equation. Those for the retraction phase describe a curve and hence are at variance with this equation.   The departure is more severe the greater the hysteresis.   The curves for ascending and descending elongation cannot therefore be fitted to the same mathematical relationship; i.e., the shapes of the corresponding stress-strain curves are incompatible.   Failure to reach equilibrium is the obvious cause for this discrepancy.   Not only is the descending curve called into question on this account; that for the ascending phase of the cycle is rendered equally suspect.   This point will receive further emphasis as the analysis of the results proceeds.

<p align="center">TABLE IV</p>

<p align="center">SUMMARY OF PRINCIPAL RESULTS FOR UNSWOLLEN POLYMERS
(STANDARD PROCEDURE)</p>

Sample	° C	$2C_1$, kg cm^{-2}	$2C_2$, kg cm^{-2}
NR-1	34	0.90	1.42
NR-1	59	0.88	1.28
NR-2	34	1.52	1.40
NR-3	34	1.92	1.60
NR-3	59	2.06	1.54
NR-4	35	2.00	1.50
NR-6	34	2.00	2.00
S-1	30	0.70	0.62
S-1	94	0.88	0.62
S-1	149	0.98	0.60
S-2	30	1.00	0.80
B-1	49	1.24	1.50
PMMA	145	1.00	4.80
PMMA	175	0.60	2.60
PEA	0	1.12	1.26
PEA	49	1.54	0.72
PEA	95	1.56	1.40

For the purpose of characterizing the behavior exhibited by various samples, the slopes of the linear plots obtained with ascending elongation, such as are shown in Figure 5, have been taken to represent the apparent value of $2C_2$. The intercepts may likewise be considered to represent *apparent* values of $2C_1$. However, the evident hysteresis forbids attachment of more than relative significance to this quantity.   Table IV summarizes principal results for unswollen polymers, the values of $2C_1$ and $2C_2$ having been derived from plots such as are shown in Figure 4.   The values given represent averages for three or more experiments.   The intercepts $2C_1$ serve to indicate relative degrees of crosslinking.   The values of $2C_1$ listed for the highly hysteretic PMMA probably should be discounted altogether in this regard.

Before turning to analysis of the results presented in Table IV, the bearing of the data assembled in Table III on the validity of the standard procedure deserves inspection.   Comparison of the first two entries with the third for NR-6 demonstrates that the value found for $2C_2$ using a separate specimen at each elongation differs little from that obtained using the standard stepwise procedure.   The results given for NR-3, these having been obtained using the latter procedure, show $2C_2$ to be insensitive to the time interval employed at each step.   Sample NR-6 at 59° C in air, on the other hand, displays an increase

in $2C_2$ (and in the hysteresis as well) with prolongation of the time interval from 3 to 30 min. Appreciable chemical degradation of this sulfur vulcanized sample (Table I) occurred during the course of the latter experiment involving exposure to air at 59° C for a total of about 10 hr. Thus, the swelling ratio in benzene increased from $1/v_2 = 5.46$ before the experiment to 5.80 afterwards. Deterioration of the primary network structure in the course of an experiment must obviously contribute an increase in $2C_2$ when, as in the standard procedure, a single sample is used throughout the stress–strain cycle.

PMMA at 145° C displays a decrease in $2C_2$ with duration of the time interval. That the variation cannot be ascribed to chemical alteration of the network, was demonstrated by repetition of a 3 min interval experiment on the sample previously carried through the 30 min run, sufficient time having been allowed between experiments for recovery of the initial L_0. The previous 3 min value (4.80) for $2C_2$ was found.

We conclude from these experiments that the values obtained for $2C_2$ are insensitive to details of the procedure. Specifically, the use of a single sample throughout the cycle of successive elongations does not seriously affect the value obtained for C_2. The particular time interval adopted for the standard procedure is only of minor consequence. Chemical degradation in the course of the experiment does, however, tend to increase both the hysteresis and the values of $2C_2$.

Correlation of C_2 with hysteresis.—The most striking feature of the results summarized in Table IV is the direct correlation of the values of $2C_2$ with the hysteresis exhibited by the five polymer systems investigated (see Figures 1, 4, and 5). Thus, the silicone polymers yield the lowest values for $2C_2$, and PMMA the highest, with NR, B, and PEA [poly-(ethylacrylate)] occupying intermediate positions.

An increase in temperature from 145° C to 175° C decreases $2C_2$ for PMMA, as would be expected from consideration of the rapid increase in internal mobility with temperature in the vicinity of the glass transition temperature T_g, which for the crosslinked PMMA is *ca.* 110° C. Similarly, $2C_2$ for PEA $(T_g \cong -25°$ C) decreases markedly from 0° C to 49° C. The increase at 95° C is believed to have been caused by chemical alteration of the crosslinked structure at this temperature. Parallel changes in hysteresis are evident in Figure 5.

The temperature range over which natural rubber can be investigated is restricted owing to its sensitivity to chemical degradation. Comparison of the $2C_2$ values given in Table IV for 34° and 59° C suggests a small decrease with temperature. For the silicone on the other hand no perceptible change with temperature was observed.

An increase in the degree of crosslinking diminishes the hysteresis indicated by the divergence between plots for increasing and decreasing elongation; the results for NR-1 and NR-3 shown in Figure 5 are illustrative. As is apparent from the data presented in Table IV for natural rubber samples NR-1 to NR-4 at 34° C, the values for $2C_2$ taken from the ascending phase of the elongation cycle are insensitive to the degree of crosslinking. The same conclusion was reached by Gumbrell, Mullins, and Rivlin[13]. These four samples were crosslinked with γ radiation using the various dosages recorded in Table I. Increase in crosslinking with dosage is manifested in the values for $2C_1$ in the third column of Table IV.

In view of the apparent dependence of the hysteresis on the degree of crosslinking, it becomes important to choose comparable degrees of crosslinking in

order to achieve a proper comparison of values of $2C_2$ with the hysteresis. In the case of S-1 for example, the degree of crosslinking as judged by the value of $2C_1$ is less than that for NR-1, the rubber sample having the lowest degree of crosslinking. Nevertheless, the hysteresis for S-1, as well as the value of $2C_2$ is much less than that for NR-1.

The somewhat larger value of $2C_2$ for NR-6 compared with that for NR-3, and its higher hysteresis as well, may be related to the method of crosslinking, which in this instance involved conventional chemical vulcanization with sulfur and an accelerator (Table I). Either a greater susceptibility to bond rupture giving rise to "chemical" stress relaxation, or enhancement of hysteresis
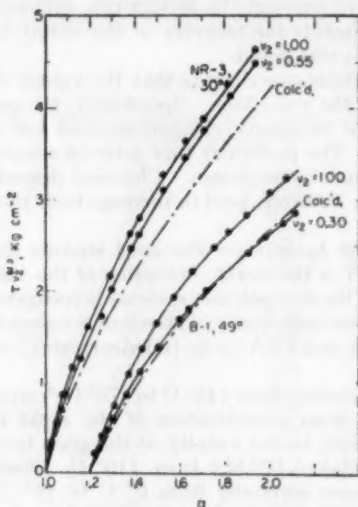
Fig. 6.—Effect of dilution with n-hexadecane on the stress-strain curve (elongation phase of the standard procedure). Broken lines are calculated from equilibrium degree of swelling using Equation (3'). Results for B-1 shifted 0.2 abscissa unit to the right.

due to the incorporation of sulfur and additional chemical alterations introduced by the vulcanization ingredients used, may be responsible for the difference, which in any event is not large.

Similarly, the silicone sample S-1 crosslinked with benzoyl peroxide displays a somewhat smaller value for $2C_2$ compared with that for S-2, the latter having been crosslinked with γ radiation. Inferior chemical stability of the latter network is suggested.

The close connection between the value of $2C_2$ and the hysteresis of the sample under conditions of experiment is further emphasized by results presented below.

Effect of dilution.—Stress-strain curves for NR-3 and B-1, diluted in each case with n-hexadecane, are compared in Figure 6 with corresponding curves for the undiluted ($v_2 = 1.00$) polymers. The stress τ has been multiplied by $v_2^{\frac{1}{3}}$ in deference to the molecular theory, according to which $\tau v_2^{\frac{1}{3}}$ should be invariant to swelling for a given value of extension α relative to the rest state for the swollen sample [see Equation (3')]. The "calculated" curves represented

by broken lines have been derived from Equation (3′) using the values of the network parameters $(\nu/V)\langle\alpha\rangle^2$ given in Table II. These values, it will be recalled, were calculated from the degree of swelling and the thermodynamic parameters χ_1 for the relevant solvent-polymer systems. The principal uncertainty in this calculation rests on the value of χ_1. Alteration of χ_1 by the acknowledged experimental error of ±0.01 in this quantity shifts the ordinate values for each calculated curve by approximately ±7%.
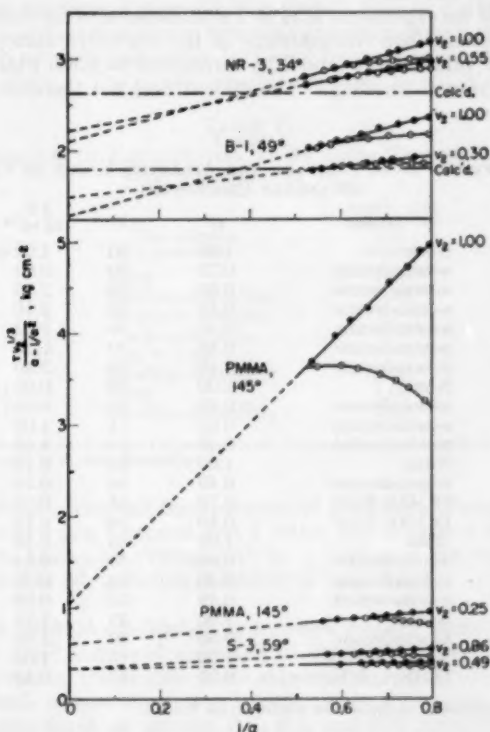
FIG. 7.—Reduced stresses plotted against $1/\alpha$ for NR-3, B-1, PMMA, and S-3 with and without diluent (n-hexadecane for NR-3, B-1, S-3; diethyl phthalate for PMMA). Data for NR-3 and B-1 are identical with those shown in Figure 6. Horizontal broken lines indicate calculated values. Points ● for elongation phase and ○ for retraction phase of the standard procedure cycle.

The same results are reproduced in Figure 7, where $\tau v_2^{\frac{1}{3}}/(\alpha - 1/\alpha^2)$ is plotted against $1/\alpha$. Also included are results for PMMA and silicone S-3. The calculated value of the ordinate is indicated in each case by a broken horizontal line, which corresponds to the "calculated" curve in Figure 6. Close approach to the molecular theory with dilution is conspicuously evident in both figures.

Additional results are summarized in Table V. Incorporation of diluent invariably lowers $2C_2$. Similar observations were reported by Gumbrell, Mullins and Rivlin[13].

The decrease in $2C_2$ is greater the higher the dilution. The value of C_2 does not, however, vanish even at degrees of swelling approaching the maximum. Likewise, hysteresis, though reduced, remains in evidence, as indicated by the divergence of the retraction from the extension curves shown in Figure 7. The effect of dilution is most marked for the highly hysteretic PMMA. The low molecular weight polymer DC-200 reduces C_2 for the silicone polymer to about the same degree as n-hexadecane; the influence of dilution appears not to be peculiar to the diluent used.

Repetition of the experiment at $v_2 = 1$ after removal of the diluent invariably yields a stress-strain loop characteristic of the unswollen state; both the hysteresis and the value of $2C_2$ (and $2C_1$) correspond to those which would have been obtained prior to swelling. The diluent does not therefore permanently alter the structure.

TABLE V

EFFECTS OF DILUTION ON THE APPARENT VALUE OF C_2
(STANDARD PROCEDURE)

Sample	Diluent	v_2	° C	$2 C_1$, kg cm^{-2}	$2 C_2$, kg cm^{-2}
NR-3	None	1.00	30	1.92	1.60
NR-3	n-hexadecane	0.70	30	2.00	1.20
NR-3	n-hexadecane	0.60	30	2.10	1.04
NR-3	n-hexadecane	0.55	30	2.10	1.00
NR-3	n-hexadecane	0.50	30	2.02	1.18
NR-3	n-hexadecane	0.46	30	2.20	0.80
NR-3	n-hexadecane	0.40	30	2.40	0.44
NR-7[a]	None	1.00	34	0.90	1.50
NR-7	n-hexadecane	0.86	34	0.96	1.00
NR-7	n-hexadecane	0.61	34	1.00	0.56
NR-7	n-hexadecane	0.40	34	1.00	0.30
S-1	None	1.00	34	0.72	0.58
S-1	n-hexadecane	0.49	34	0.70	0.22
S-1	DC-200 fluid[a]	0.79	34	0.70	0.40
S-1	DC-200 fluid[a]	0.40	34	0.72	0.10
S-3[a]	None	1.00	145	0.40	0.56
S-3	n-hexadecane	0.86	59	0.34	0.26
S-3	n-hexadecane	0.49	59	0.36	0.08
S-3	n-hexadecane	0.49	35	0.30	0.04
B-1	None	1.00	49	1.24	1.50
B-1	n-hexadecane	0.30	49	1.50	0.40
PMMA	None	1.00	145	1.00	4.80
PMMA	Diethyl phthalate	0.25	145	0.40	0.50

[a] Prepared by crosslinking in the swollen condition; see Table I.

These observations are immediately compatible with the hypothesis that the C_2 term arises in the analysis of experimental data as a consequence of failure to reach equilibrium, and that its magnitude depends directly on the hysteresis exhibited by the sample. Against the possible contention that the isotropic expansion accompanying swelling produces an alteration of the configuration of the chains of the network which somehow engenders better agreement with theory, samples NR-7 and S-3 were prepared by crosslinking diluted specimens (see Table I). The chains of these networks are in random configurations at the volume fractions $v_2 = 0.40$ and 0.49, respectively. At $v_2 = 1.00$, achieved by removal of diluent after crosslinking, the network chains are forced into more compact configurations than would prevail for the free chains at the same temperature. If the foregoing alternative hypothesis were valid, the $2C_2$ values at the volume fractions $v_2 = 0.40$ and 0.49, respectively,

should correspond to those for undiluted NR-3 and S-1; upon removal of diluent even higher values of $2C_2$ should be expected. Such is not the case. The $2C_2$ values depend solely on the dilution and not perceptibly on the volume at which crosslinking was performed.

Finally, we note that the apparent values of $2C_1$ change somewhat with dilution. Where the hysteresis (and $2C_2$) is not excessive, they tend to increase somewhat with dilution. For PMMA, however, the reverse is true. No particular significance is attached to this variation, for if C_2 is a fiction of the impediments to attainment of equilibrium then C_1 may be distorted simultaneously. It is important however to note that grave errors may arise in attempts to evaluate the network parameter $(\nu/V)\langle\alpha\rangle^2$ from stress measurements using Equation (3) or (5). The closest possible approach to equilibrium should be

TABLE VI

RESULTS OF EQUILIBRATION BY SWELLING TEMPORARILY
WITH n-PENTANE AT $39°$ C [a]

Sample	Equilibration treatment	Approx v_2 at max swelling with pentane	$2 C_2$, kg cm^{-2}
B-2	None	1.00	1.20
B-2	Swelling-deswelling	0.20	0.50
B-2	Constant dilution, n-hexadecane, $v_2 = 0.30$		0.36
S-1	Swelling-deswelling	0.20	0.16
NR-3	None	1.00	1.60
NR-3	Swelling-deswelling	0.50	1.20

[a] Lengths measured at fixed tensions in each instance, instead of at fixed lengths as per standard procedure. Time interval 2 hr at each elongation.

achieved, preferably through incorporation of a diluent. Results such as are shown in Figures 6 and 7 suggest that a better approximation to this quantity may be had by taking an average $\tau v_2^{\frac{1}{3}}/(\alpha - 1/\alpha^2)$ over the range $\alpha = 1.5$ to 2.0, in preference to extrapolation according to Equation (5).

Attempts to establish equilibrium by transient swelling under fixed tension.— As shown by Gee[10] improved approach to equilibrium may be achieved by temporarily swelling the sample while suspending a fixed load, using for this purpose a volatile diluent which may be removed by evacuation. Such experiments were carried out on samples B-2, S-1, and R-3 using n-pentane as the transient diluent. The tension being fixed during each cycle of swelling and deswelling, the stress-strain curves were established by conducting experiments at a sequence of tensions rather than at incremental elongations (see experimental section). Results are presented in Figure 8 and in Table VI. For purposes of comparison, the same procedure was applied to unswollen samples (open circles in Figure 8) and to a sample of butyl rubber permanently swollen by n-hexadecane (half-filled cricles) with omission of the pentane swelling and deswelling cycle. The concentration at maximum dilution with pentane, given in the third column of the table, was estimated from the maximum length of the sample during the swelling-deswelling cycle, the appropriate theoretical relationship being used[3].

The diminution of $2C_2$ resulting from swelling and deswelling clearly supports the hypothesis that deviation of the stress-strain curve from the simple

form predicted by the molecular theory is largely, if not entirely, a consequence of the difficulty of achieving states of equilibrium. The irreversible net increase in elongation (at fixed tension) upon swelling and deswelling admits of no other explanation.

The results presented do not, unfortunately, eliminate the possible reality of a small residual C_2 at equilibrium. The cycle of swelling and subsequent removal of n-pentane required about two hours, hence the necessary measurements for definition of the stress-strain curve entailed operations on a single sample for a period of 20 hr. Irreversible alterations of the structure brought about by spurious degradative processes are difficult to suppress altogether throughout such protracted experiments. Natural rubber and butyl rubber are particularly vulnerable in this respect. Stress relaxation resulting from structural changes in the course of such experiments will of course raise the apparent values for $2C_2$. The values recorded in Table VI should therefore be regarded as upper limits.
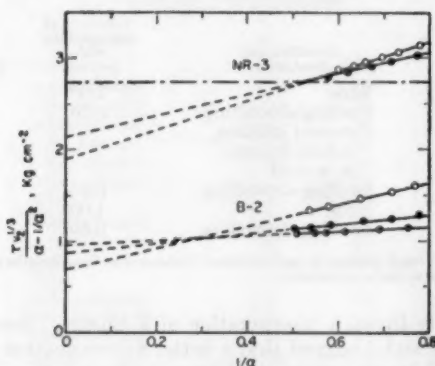
Fig. 8.—Reduced stress plotted against $1/\alpha$ for NR-3 and B-2 at 39° C. Time interval 2 hr at each elongation. Swelling-deswelling procedure, ●; unswollen polymer, ○; B-2 permanently swollen with hexadecane ($v_1 = 0.30$), ◐; Horizontal broken line for sample NR-3 calculated from equilibrium degree of swelling using Equation (3′).

CONCLUSION

The body of evidence presented above shows beyond question that the deviation of the stress-strain curve from the form predicted by the molecular-kinetic theory of elasticity is in large measure a consequence of the experimental difficulties attending establishment of equilibrium. Any alteration of composition or experimental conditions which substantially reduces the hysteresis also lowers the apparent value of C_2. The influence of diluents in this respect is particularly noteworthy; their pronounced effect on the values obtained for C_2 admits of no other explanation. Even at the highest degrees of swelling investigated (near the limits of swelling equilibrium with n-hexadecane), the value of C_2 does not appear to have reached a limit. Hence, if greater dilution were possible, a further decrease in C_2 could be anticipated. In the case of the silicone polymer at maximum swelling, C_2 is already barely perceptible. The evidence strongly suggests, therefore, that C_2 would become quite negligible if complete relaxation to equilibrium states could be achieved at each elongation.

The results which have been presented repudiate an alleged major shortcoming of the theory of rubber elasticity.

SUMMARY

According to the molecular theory of rubber elasticity, the stress τ is related to the relative length α in simple extension according to $\tau = kT(\nu/V)\langle\alpha\rangle^2 (\alpha - 1/\alpha^2)$, where $(\nu/V)\langle\alpha\rangle^2$ is a parameter of the network structure. Improved agreement with experiment has been claimed through use of the relation $\tau = (2C_1 + 2C_2/\alpha)(\alpha - 1/\alpha^2)$ which contains the additional parameter C_2. In order to explore factors affecting this theoretically inexplicable term, stress-elongation measurements were performed on networks prepared from natural rubber, Butyl rubber, poly-(dimethylsiloxane), poly-(ethyl acrylate), and poly-(methyl methacrylate) under a wide range of experimental conditions. Results may be summarized as follows: (1) the C_2 term offers improved agreement over the extension phase of an elongation cycle, but not for the subsequent retraction phase; (2) apparent values of C_2 (determined on extension) vary widely from one polymer to another, increasing with hysteresis and with proximity to the glass transition temperature; (3) they are insensitive to the degree of crosslinking; (4) C_2 is markedly reduced by permanently swelling the network with a diluent, or by swelling and deswelling the sample at each tension; (5) incorporation of diluent prior to establishing a network by crosslinking with gamma radiation likewise lowers C_2, the value characteristic of the unswollen polymer being restored upon removal of the diluent. The results demonstrate that the controversial C_2 term arises from the difficulty of attaining elastic equilibrium; under ideal experimental conditions the value of this parameter becomes negligible. An alleged limitation of the theory of rubber elasticity is thus refuted.

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MEASUREMENT OF THE DYNAMIC MODULUS OF RUBBER AT VERY SMALL AMPLITUDES WITH AN OPTICAL INTERFEROMETER *

N. M. BOROVITSKAYA

A method of measuring very small differences of optical path using light modulation by an interferometer has been described[1-3]. This enables one to measure amplitudes of mechanical vibrations of the order of 0.01 A or even smaller. We have used this method to measure the dynamic modulus of rubber at very small amplitudes. It is desirable to use this method for measuring the dynamic modulus of rubber and other highly elastic substances, firstly because in accuracy and simplicity it has certain advantages over existing acoustic methods. In the second place, it enables one to work at very small amplitudes and, in association with other methods, over a very wide range of amplitudes of deformation. This is of interest in connection with the general theory of the dynamic properties of rubber, and in particular, for checking the linearity of these properties, that is, the independence of the modulus and the loss on the amplitude, in particular for filled rubbers[4, 5].

We will briefly describe the apparatus with which the measurements were made. It consists of a Michelson interferometer and a source of monochromatic light. The interference pattern (lines of equal width) is projected onto the cathode of a photomultiplier. The output of the photomultiplier is fed to the input of a narrow-band filter, to the output of which the measuring instrument is connected. The mirror on the interferometer is set up so that the whole of the interference pattern, or the greater part of it, is uniformly illuminated. If now one of the mirrors vibrates with a frequency ω and an amplitude of z, then the difference in path between the interference beams will vary with a frequency of ω and the intensity of the light falling on the photomultiplier will also change. The current through the photomultiplier will be modulated with a frequency of ω. The first harmonic of the photocurrent will be $I_1 = A J_1$ $(4\pi z/\lambda)$, where λ is the wavelength of light; A is a coefficient depending on the intensity of the interfering beams and on their difference of path with the mirror at rest; I_1 is a first order Bessel function.

If the narrow-band filter passes a frequency ω, then the reading on the output instrument will be proportional to I_1. For $4\pi z/\lambda \leqslant 0.5$ the reading on the output instrument will, with an error of 1%, vary with the amplitude of the vibration in accordance with the equation $\alpha = Bz/\lambda$, where B is an apparatus constant, which includes A. In our conditions (wavelength of 5460 A) this relationship is correct for $z \leqslant 200$ A.

The equipment with which we worked enabled us to measure a displacement of the order of 0.001A, at frequencies of 100–10,000 cps. The rubber specimens were mounted by bonding them to a massive support (Figure 1) which was placed in one of the arms of the interferometer. Three identical specimens were tested simultaneously. An alternating voltage of frequency $\omega/2$ was applied
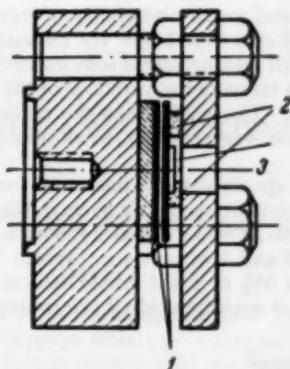
Fig. 1.—Support for mounting the specimens. *1*—Electrodes;
2—rubber specimens; *3*—mirror.

to the electrodes *1*, causing them to oscillate and stretching the rubber *2* at a frequency ω. The righthand electrode and the disc to which the rubber is bonded, are grounded, so that the rubber is outside of any electrical field which could cause electrostrictional vibrations in it. The lefthand electrode, together with the insulating disc is rigidly fixed to the base of the support. The mirror *3*, bonded to the electrode and vibrating with it, is one of the mirrors of the interferometer. Light falls on it through an opening in the disc.

Measurements gave the amplitude of deformation of the rubber. The amplitude of the force was found by calculation (the potential applied to the electrodes, the area of the electrodes, and the gap between them being known). The dynamic modulus was determined as a ratio of the amplitude of the mechanical stress to the amplitude of deformation. We measured the modulus of four rubbers. No. 1 was a vulcanized natural rubber, filled with chalk; No. 2 a vulcanized natural rubber, without filler; No. 3 vulcanized natural rubber filled with carbon black: No. 4 SKS-30 vulcanized rubber filled with carbon black. Cylindrical specimens 2, 4, 6 and 8 mm diameter were prepared from each rubber. All of the measurements were made at a constant temperature of
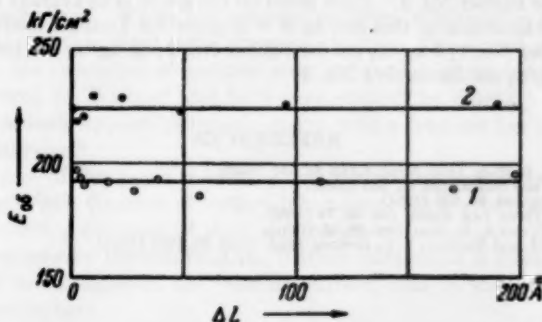
Fig. 2.—Variation of modulus with amplitude of deformation. *1*—rubber No. 3; *2*—rubber No. 4.
Ordinate: modulus of specimen in kg/sq cm.

20° C. For simplicity and greater reliability of calculations of the modulus, the frequencies (300–500 cps) were below the resonance frequency of the rubber-electrode system. All measurements were carried out at these frequencies. An attempt was made to measure the variation of the modulus of one specimen (No. 3) with frequency. Up to 8000 cps the modulus was constant within 10%, but then increased very sharply when the frequency was increased further.

The modulus of the specimens was measured for deformation amplitudes between 1 and 100 A, which means, for an average thickness of 2 mm, a relative deformation of 5×10^{-6} to 10^{-3}%. Figure 2 shows the variation of the modulus of specimens of rubber 3 and 4 with strain. It will be seen that the modulus remains constant within 5% over the whole deformation range. Similar results were obtained for all specimens of all the rubbers.
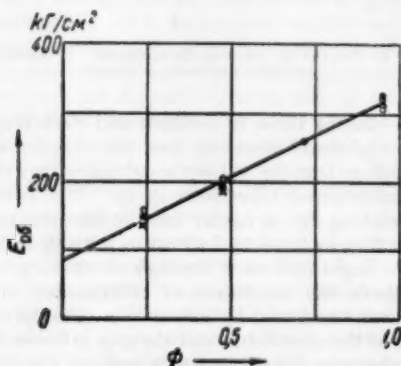
Fig. 3.—Variation of modulus with shape factor. Ordinate: modulus of specimen in kg/sq cm. Abscissa: shape factor.

Young's modulus for the materials can be worked out from the results using the methods proposed by Bartenev and Novikov[6]. For this, we plotted the modulus of a specimen against the shape factor (S) (ratio of the cross sectional area to the area of the lateral surface of the specimen). Figure 3 shows this variation for rubber No. 3. Each point on the graph is as average from several tests. Extrapolation of this line to $S = 0$, gives for Young's modulus 9 kg/sq cm for rubber No. 1; 3 kg/sq cm for rubber No. 2; 85 kg/sq cm for rubber No. 3 and 90 kg/sq cm for rubber No. 4.

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STRESS WAVES AND FRACTURE SURFACES *

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INTRODUCTION

The fracture surfaces of brittle materials have been widely studied in an attempt to explain what happens when such a material breaks. The similarity of fracture markings in brittle materials of otherwise very different physical properties[1] indicates that some basic process operates to produce them.

There are several well-defined types of fracture marking in noncrystalline materials.

(1) Those associated with simple roughness or smoothness of the surface. "Mirror" surfaces are optically smooth; "mist" surfaces are rough on a very fine scale; "hackle" surfaces are rough on a gross scale and generally display directional features.

(2) Conic lines; i.e., hyperbolic, elliptic, or parabolic markings in the surface which evidently mark the intersection of fractures spreading outwards from different focuses[1].

Smekal[2] has shown how interaction between the advancing fracture and inhomogeneities within the body could lead to the observed effects. (That such microscopic inhomogeneities exist within brittle materials is required by the theory of fracture developed by Griffiths[3] for glass.) The region of high stress surrounding the initial fracture induces secondary fracture at points ahead of the tip where inhomogeneities superimpose their own stress concentration. If the inhomogeneities are closely spaced, the effect will be a progressive roughening of the surface; if widely spaced, the separate secondary fractures may be resolvable, as in the case of conic markings. The higher the stress in the body the larger will be the fracture's sphere of influence, the wider the region subjected to secondary fracture, and, thus, the rougher the surface.

(3) Wallner lines. These are periodic markings attributable to the interaction of the fracture front with ultrasonic waves. The waves are probably produced by the relaxation of material after the passage of the fracture. They were discovered by Wallner[4] and have been studied by Smekal[5]. The interaction of *externally* applied ultrasonic waves with a fracture has been demonstrated by Kerkhof[6].

The purpose of this paper is to show how Wallner lines produced in the low temperature brittle fracture of certain inhomogeneous (carbon-filled) rubbers provide convincing evidence of their mechanism of formation. A distinction is also drawn between the nature of the Wallner lines found in glass, where they form actual undulations in the fracture surface, and in the inhomogeneous material studied here.
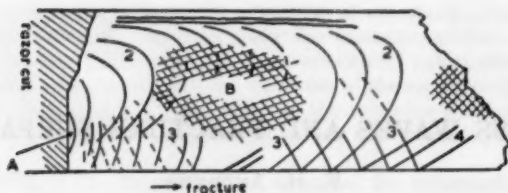
FIG. 1.—Sketch of fracture surface, showing Wallner lines. (Wave systems numbered for comparison with loci of Figure 6. *A*, mirror zone; *B*, hackle region.)

PRODUCTION AND CHARACTERIZATION OF WALLNER LINES IN INHOMOGENEOUS RUBBER

The observations were made upon frozen rubbers containing 30% by weight of colloidal carbon black. The fracture surfaces show markings familiar in glass *etc.*, such as a semicircular "mirror" initiation region, "mist" and "hackle." In addition, systems of wavelike markings are found which are sometimes very well defined. Figure 1 illustrates part of the fracture surface (2 cm by 0.2 cm) of a strip of material which had been notched with a razor blade and broken in flexure. The semicircular initiation zone is at the left, the fracture spreading from the razor notch. Two large central regions of gross "hackle" are surrounded by smoother areas in which the Wallner lines are readily visible.

Micrographs of the waves are reproduced in Figures 2 and 3. The former shows three systems of circular waves near to the initiation, one confocal with the fracture front, and two with centers displaced, respectively, above and below the fracture center. Figure 3 shows an edge reflection occurring at that side of the specimen in tension during flexure.
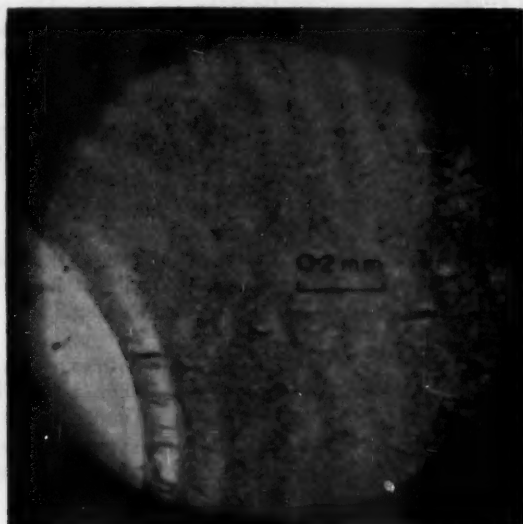
FIG. 2.—Micrograph showing Wallner waves and part of initial mirror zone.
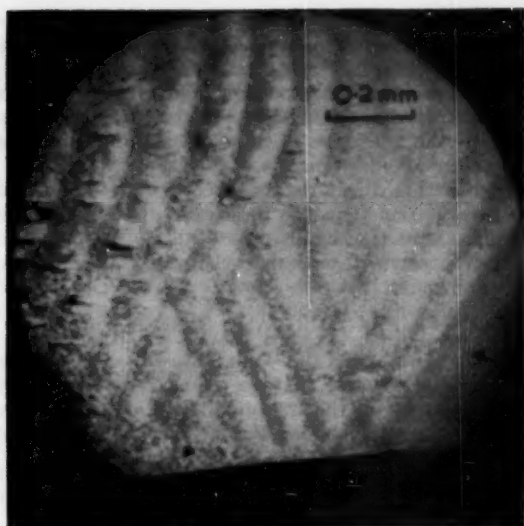
Fig. 3.—Micrograph showing edge reflection of Wallner waves.

The nature of the Wallner lines has been investigated by interference microscopy, as described in the Appendix.

Figure 4 is an interference micrograph with fringes running across three of the Wallner waves which lie top right to bottom left of the picture. In the

Fig. 4.—Interference micrograph of Wallner waves.   A, mirror regions; B, mist regions.

dark, upper portion of the micrograph the specimen and reference surfaces are actually in contact. Well defined fringes traverse the mirror regions, A, but regions B are so rough, on a fine scale, that the fringes are severely broken up.

These are regions of "mist" and, possessing low reflectivity, appear as dark bands in the ordinary sufrace micrograph (Figure 3). The upper part of Figure 4 shows how the roughness of these regions prevents intimate contact between them and the reference surface.

Incipient hackle occurs within the regions of mist (see Figures 2 and 3) and there is a strong suggestion that it is most severe at the intersection of such regions. Although alternating bands of smooth and rough surface have previously been noted[1] in polymethyl methacrylate, they have not been associated with Wallner phenomena.

FRACTURE AND STRESS

The first distinctive feature of the Wallner waves is the intersection of wave fronts. This immediately shows that they do not merely represent periodic (*i.e.*, "stick-slip") behavior of the fracture itself; intersecting *fracture* fronts can only meet along a single line, and there could be no overlapping of two or
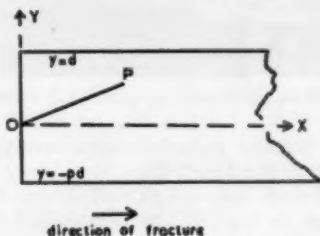
FIG. 5.—Diagram used to discuss relationship of stress wave and fracture front.

more systems of waves. Evidently, there exists a periodic variation of state within the material prior to fracture which is effectively "photographed" as the fracture passes.

Smekal[2] has suggested that the higher the local stress around the fracture in an inhomogeneous material, the rougher will be the resulting surface. He attributed mist and hackle to increasing orders of local stress (see introduction). A similar mechanism to Smekal's has been advanced[7] to account for other rupture phenomena in carbon-filled material. It seems clear that the surface waves described here represent periodic variations of the *state of stress* in the body prior to the passage of the fracture. They are true Wallner phenomena *arising from the interaction of the fracture front with stress waves within the body*.

It is important to notice that these stress waves cannot be standing waves since these could not lead to a distorted edge reflection such as is seen in Figure 2, where the axis of symmetry of the wave pattern is not normal to the edge.

SOURCE OF THE STRESS WAVES

Because the velocity of elastic waves is typically greater than that of fracture and the stress waves are presumably traveling in the same direction as the fracture, their possible sources are limited. The simplest suggestion is that advanced by other workers (see introduction) that the region immediately behind the fracture tip is in oscillation. Calculation shows that such an oscillation could account for the observed disposition of the fracture waves.

Let the origin of the circular fracture front be at 0, at one end of the fracture surface bounded by parallel edges at $y = d$, and $y = - pd$ where p is a fraction (Figure 5). Assume that a stress pulse is generated some small distance ϵ behind the fracture front along a circular arc concentric with the front so that both fracture and stress waves have the same apparent origin 0. Let the stress pulse overtake the fracture front at an arbitrary distance R from 0. Let the velocities of the stress pulse and the fracture front be, respectively, v_1 and v_2, and let $v_1/v_2 = \alpha$.

We wish to find the possible loci of intersection of the stress wave and the fracture front. One obvious locus is a circle center 0 and radius R. If ϵ is zero (oscillation *at* fracture tip) no corresponding "fracture wave" will appear. Other intersection loci will arise from reflections of the stress pulse at both edges of the fracture surface. That arising from the first reflection from the edge at $y = d$ is given by the equation,

$$(\alpha^2 - 1)\left\{ r - \frac{R\alpha}{\alpha + 1} \right\}^2 = 4d(d - y) + R^2 \frac{(\alpha - 1)}{(\alpha + 1)} \tag{1}$$

where $r = (x^2 + y^2)^{\frac{1}{2}}$ is the distance from the origin. That from the first reflection at the edge $y = - pd$ is obtained by replacing d by $-pd$; that from the second reflection from the edge at $-pd$ by replacing d by $(d + pd)$ and so on.
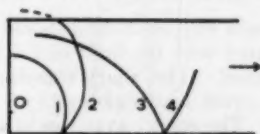
Fig. 6.—Calculated intersection loci with $\alpha = 2.0$. (1) Circle, center 0; (2) arising from first stress reflection from lower edge; (3) arising from first stress reflection from upper edge; (4) arising from second stress reflection from lower edge.

Figure 6 shows the curves for four intersection loci as indicated, using a convenient, arbitrary value for R. It will be seen that the observed Wallner waves of Figure 1 are very similar in nature and relationship to these calculated loci. Discrepancies that do exist are probably due to variations in fracture velocity. The actual wave pattern, of course, requires a succession of stress pulses.

Further information can be obtained from Figure 3, since the angles of incidence and reflection of these waves depend upon the numerical factors in Equation (1).

Differentiation of Equation (1) with respect to y,

$$\frac{dx}{dy} = \frac{-1}{x}\left\{ y + \frac{2d}{\alpha^2(1 - R/r) + \alpha R/r - 1} \right\} \tag{2}$$

gives the slope of the Wallner lines arising from the first stress reflection from the edge $y = d$. The corresponding Equation (2a) for the second reflection of this pulse (from the opposite edge) is obtained by replacing d by $(d + pd)$.

If we now set $y = - pd$, we can find the angles (θ and ϕ to the normal) at which these two Wallner lines meet the lower edge. In order to obtain explicit results we must obtain the value of x/d from the fracture specimen, and measure the tangents dx/dy of θ and ϕ. With

$$x/d = 4; \theta = 15°; \phi = 40°$$

agreement between Equations (2) and (2a) is found only if p is 0.62. In support of this value, the fracture origin is closer to the lower rather than the upper edge of the specimen, as Figure 1 will show, though some way along the specimen the apparent origin of the fracture front may no longer be the fracture origin.

With this value of p the only remaining unknowns are R/r and α. At large R, the ratio R/r will be close to unity. A first approximation to its value may be found from Equation (1) by setting $x \cong r \cong 4d$, and choosing $\alpha = 2$. This gives $R/r = 0.85$.

Using this value in Equation (2) the ratio of the velocities is found to be

$$\alpha = 1.91$$

Clearly, successive approximations of R/r and α could be obtained, but the final value would not be very different.

It is concluded, then, that for frozen rubber

(a) the simple theory of an oscillation in the relaxing zone of the fracture is sufficient to account qualitatively for the Wallner phenomena;

(b) the ratio of the fracture velocity to the speed of stress propagation (over a particular region of the fracture) was approximately 1:2.

CAUSE OF THE OSCILLATING FRACTURE

There is no obvious reason why oscillation should occur behind the fracture front. Its onset is associated with the limit of the initial semicircular mirror zone, which is sharply defined. This sharp transition seems to be caused by some definite self-induced event which also sets off the oscillations. It may arise in the following way. The energy available in a large test piece to a small growing crack, per unit increase of its length, is proportional to its length[8]. Thus, as the fracture spreads outwards from its origin it will tend to accelerate in order to utilize the increasing energy supply. There probably exists a limiting velocity for the fracture, low compared with the velocity of sound, and when this velocity is reached by the growing fracture it will become unstable and adopt one method or another of dissipating the excess energy. Deviation of the fracture, branching or oscillation could arise in this way. Possibly all of these occur, but to differing degrees governed by unknown factors. The suggestion is supported by Smekal's observation that if a fine incision is made in a glass rod prior to fracture the initial mirror zone can be greatly increased. In this case a comparatively small amount of energy is stored in the test specimen before fracture occurs and the fracture may never attain its limiting velocity. In a similar way very slow fracture can be made to yield unlimited mirror regions where fast fracture of the same materials show early breaking up of the surface[1].

It will be recognized that such a theory of fracture is in many respects equivalent to that of Smekal. It suggests, however, that at high rates of propagation the factor determining the fracture path is not so much the stress concentration, but rather the excess energy of the fracture. This makes possible a qualitative explanation of such features as branching, oscillation, and deviation of the fracture from the path of minimum energy.

. CONCLUSION

The instability of a fast moving fracture possessing excess energy can account qualitatively for features not explained by the simple theory[2] of brittle fracture

in inhomogeneous materials.   In particular it is a likely source of stress waves which interact with the fracture front to produce the Wallner lines observed in samples of frozen rubber.

SUMMARY

Surface markings observed in the brittle fracture of certain frozen rubbers display striking, wavelike characteristics.   They have been identified as "Wallner" lines, caused by the interaction of the fracture front with stress waves emanating from the region of the fracture front itself.   These oscillations are possibly caused by the supply of excess energy to the fracture tip.

A value of approximately $1:2$ is obtained for the ratio of fracture velocity to wave velocity.

APPENDIX

A light brass sleeve, 0.5 in. long, was machined to make a smooth push fit over the barrel of a 4-mm microscope objective.   The sleeve was closed by an ordinary microscope cover glass, lightly cemented on to its lower end.   The space between the objective lens and the cover glass was filled with a drop of immersion oil.   This prevents reflection from the upper surface of the glass, while accommodating relative movement between it and the lens (see Figure 7).
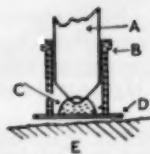
FIG. 7.—Interference microscope.   A, microscope objective; B, brass sleeve; C, immersion oil; D, glass disk; E, specimen.

A source of carefully alined, monochromatic light, and ordinary normal-incidence reflection equipment are all that are now required.   The specimen is focused with the cover glass pushed well up towards the lens, and the sleeve is then slid gently down, refocusing as necessary, until thin-film Fizeau fringes appear, caused by interference between the specimen and the lower surface of the cover glass.   The reflectivities of the rubber surface and the glass are well matched, and good results are obtained.

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DETERMINATION OF RELATIVE DAMPING
AT VARIOUS PRESTRESSES *

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INTRODUCTION

In the evaluation of the plastic-elastic properties of vulcanizates, we cannot rely solely upon static methods, but must employ dynamic testing as well. Here we must distinguish between free vibration, in which the material is stressed for brief periods only, and forced vibration, in which the vibration amplitude is held constant for a longer time.

In both cases, the rubber technologist is interested in two measurements:

1. The dynamic modulus, which establishes the stiffness of the material under dynamic stress.
2. The energy balance in the vibration process. Part of the energy which is put into the test piece is converted into heat and is lost from a mechanical viewpoint. The greater this portion of the energy, which is designated as the damping, the higher is the plasticity of the material.

No consistent conception exists with respect to the second point above. There is no doubt about the need and advisability of making such energy-balance measurements. Thus a whole series of instruments have been developed for the purpose of measuring these characteristics. Every apparatus supplies, however, different dynamic-elastic quantities, which are very difficult to bring into correlation.

In the present work, we deal only with forced vibration and make use of the damping apparatus developed by Roelig and Heidemann. The method of its operation has been adequately described[1], and we assume that it is well known.

There has always been a uniform conception of what is meant by the absolute damping of an elastic material: it is the amount of heat generated in the rubber for each vibration cycle expressed in calories or kg-cm referred to unit volume of the test specimen. On the other hand, there are several ideas as to how the data from the Roelig apparatus can be used in finding the dimensionless value of the relative damping.

As a goal for this work, we have set ourselves the task of clarifying the concept of relative damping, as well as to do the preliminary work needed for the revision of the German Industrial Standard[2], DIN 53513. The latter deals with both absolute and relative damping, and, as will be shown later, is at present inconsistent. This becomes evident if we measure the dependence of damping on the prestressing of the test specimen, and realize what effect the prestress must have on the energy balance of the vibration process. It has recently been pointed out[3] that in the case of highly elastic materials, the prestress is a parameter with a significance like that of temperature or frequency.

HISTORICAL SURVEY OF THE MORE IMPORTANT
DEFINITIONS OF DAMPING

Already in his fundamental textbook, Föppl[4] defines in addition to the logarithmic decrement the so-called relative damping with the equation:

$$\psi = \frac{H}{\alpha} \tag{1}$$

H is the area of the hysteresis loop, and corresponds to the concept of the absolute damping mentioned previously. In Figure 1, a hysteresis loop is shown, such as is obtained with the Roelig apparatus. Stress applied to the test specimen is plotted against deformation. With small amplitudes of vi-
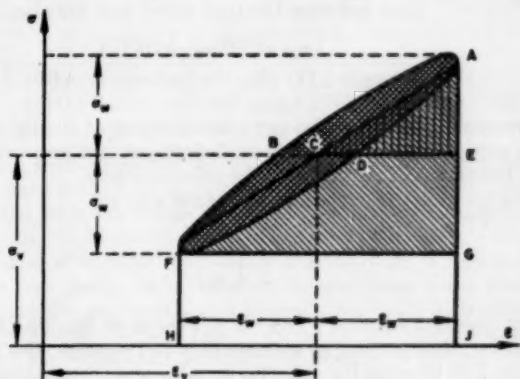
Fig. 1.—Damping ellipse for $\sigma_v > \sigma_o$ and $\epsilon_v > \epsilon_o$.

bration and where Hooke's Law applies, the hysteresis loop takes the form of an ellipse. The ellipse becomes a straight line when the system is wholly undamped.

According to Föppl, α is the maximum work of deformation which is put into the vibration element at the extreme position in the vibration. In Figure 1, α is identical with the area of triangle AFG plus the half of the ellipse ABFCA.

In his book, Lehr[5] defines in a similar way a damping-factor χ^* by the equation:

$$\chi^* = \frac{A_\rho}{A_c} \tag{2}$$

Here A_ρ again indicates the area of the damping ellipse ABFDA, and is identical with H and with the absolute damping. A_c is the small triangle ACE under the spring line. This area corresponds then to the maximum work of deformation, for an undamped spring of the same dynamic hardness as the test specimen.

Roelig extended the damping concept to measurements on rubber[1], and gives the following definitions:

Absolute damping: energy loss per vibration cycle in cm-kg, as area of the damping ellipse.

Per cent damping: ratio of the energy loss per cycle to the maximum work of deformation put into the sample per cycle.

The first concept is identical with H and with A_ρ, and the second corresponds to ψ. Both concepts have been accepted in the Standard DIN 53513. There had previously been a discussion of the matter between Roelig and Lehr[6]. Lehr contrasted two definitions, as follows:

$$\text{Damping number } \chi = \frac{\text{Work area}}{\text{Area between abscissa and the line for a loss-free spring}}$$

$$= \frac{\text{Area of ellipse ABFDA}}{\text{Triangle AFG}}$$

$$\text{Loss number } \phi = \frac{\text{Work area}}{\text{Area between the load curve and the abscissa}}$$

$$= \frac{\text{Area of ellipse ABFDA}}{\text{Triangle AFG plus the half-ellipse ABFCA}}$$

Here ϕ corresponds to ψ and the per cent damping of Roelig, but χ is not identical with any of the previously given definitions, not even with χ^*, since here the large triangle AFG is taken as the reference area.

Lehr derives the following relation between ϕ and χ:

$$\phi = \frac{2\chi}{2 + \chi} \tag{3}$$

It is an open question whether χ or χ^* or ϕ is the most significant in practice. It is clear, however, that in using ϕ, we refer only to the properties of the actual rubber specimen, but in using the damping number χ we must think of a spring of the same dynamic hardness, and which is free from damping.

Finally, the quantity ϕ was accepted in the Standard DIN 53513 under designation of relative damping:

$$D(\%) = \frac{100\,F_2}{F_1} \tag{4}$$

where F_2 is the area of the ellipse ABFDA and F_1 is the area of the triangle AFG plus the half ellipse ABFCA.

It is also stated in the section on "Definition" in the above-mentioned Standard: "Damping is the amount of mechanical energy which is transformed into heat through internal work by a material undergoing vibrational stress. This amount of energy (damping loss) is expressed in kg-cm or as a percentage of the mechanical energy which is received." The last sentence cannot be brought into agreement with Equation (4), as will be shown.

When, as is not done in the Standard, we express the relative damping by means of the phase relation δ which exists between stress and deformation, then we obtain from Equation (4):

$$D(\%) = \frac{100\,\pi \sin \delta}{\frac{\pi}{2}\sin \delta + 2} \tag{5}$$

It has been proposed by a number of authors, such as Leaderman[7], Marvin[8], Nolle[9] and more recently Kainradl[10], that in testing rubber, the concept of a complex modulus should be introduced, thus:

$$M^* = M' + iM'' = \frac{\sigma_w}{\epsilon_w} e^{i\delta} \tag{6}$$

where σ_w = stress amplitude (alternating stress), ϵ_w = deformation amplitude (alternating deformation), δ = phase displacement between stress and deformation.

The real part M' is designated as the dynamic modulus, the imaginary part M'', which is of interest here, according to Stavermann and Schwarzl[11], is the loss modulus and finally the quotient is considered to be the loss factor:

$$\frac{M''}{M'} = \tan \delta \tag{7}$$

DEPENDENCE OF RELATIVE DAMPING ON PRESTRESS AND PHASE ANGLE

Departing from Equation (4), which was obtained from geometric considerations, we have sought to derive the relative damping by direct integration. We proceeded from the verbal definition previously mentioned as appearing in the section on "Definition" of the Standard DIN 53513. This is considered to be clear and straightforward and in the following is regarded as binding.

Hooke's Law holds for vibrational deformations under small stresses—on the other hand the prestress σ_v can be made relatively large without detracting from the applicability of the Law. Then, for the stress σ and deformation ϵ we can make the statements according to Equations (8) and (9), thus:

$$\sigma = \sigma_v + \sigma_w \sin \omega t \tag{8}$$

$$\epsilon = \epsilon_v + \epsilon_w \sin (\omega t - \delta) \tag{9}$$

where σ_v is the constant prestress. (Instead of prestress, the concept average or mean stress is also useful, compare DIN 50100.) σ_w is the stress amplitude of the forced vibration. ϵ_v is the deformation caused by prestress σ_v. ϵ_w is the deformation amplitude of the forced vibration. ω is the angular frequency. t is the time.

The plus sign for σ signifies that a pressure is exerted on the test piece and the negative sign means a pull. The positive sign for ϵ corresponds to a compression of the test specimen and the negative sign indicates extension.

The sign of the work differential

$$dA = \sigma d\epsilon \tag{10}$$

is then positive for the amount of work received by the testpiece and negative for the amount of work returned to the test apparatus. The relative damping D', in the sense of the verbal definition given in the Standard, is then expressed by Equation (11). (In Equation (11) and in the following, for the sake of simplicity, the factor 100 is omitted. Since other formulas for damping are

derived than those given in Equations (4) and (5), the symbol D' will be used in the following.)

$$D' = \frac{\int_0^{2\pi} \sigma \, d\epsilon}{\int_0^{2\pi} f(\sigma \, d\epsilon) \, \sigma \, d\epsilon} = \frac{A_Z}{A_N} \tag{11}$$

whence

$$f(\sigma \, d\epsilon) = 1 \text{ for } \sigma \, d\epsilon > 0$$
$$f(\sigma \, d\epsilon) = 0 \text{ for } \sigma \, d\epsilon \leqq 0$$

A_N represents the total mechanical energy taken up by the test specimen, since the factor $f(\sigma \, d\epsilon)$ provides that dA is summed up over positive elements only. A_Z is the total energy balance of the test specimen, and is identical with the area of the damping ellipse. The amount of energy A_Z is changed to heat and the amount $A_N - A_Z$ is given back to the machine by the test piece.

The integral can be evaluated by substituting Equations (8) and (9) into Equation (11), and the expressions for D' give in Table I are thus obtained.

DERIVATION OF THE FORMULAS GIVEN IN TABLE I

Since only the differential $d\epsilon$ of the deformation appears in Equation (10), it can be seen that the predeformation ϵ_v does not enter into the calculation. Without reducing the generality, we need therefore only consider damping ellipses for $\epsilon_v = 0$ and it is necessary to study only a displacement parallel to the ordinate which corresponds to various values of σ_v (see Figures 2, 3 and 4).

Evaluation of the integral of the numerator A_Z in Equation (11) yields Equation (12):

$$\int_{\omega t_1}^{\omega t_2} \sigma \, d\epsilon = \epsilon_w \int_{\omega t_1}^{\omega t_2} [\sigma_v + \sigma_w \sin \omega t] \cos (\omega t - \delta) \, d(\omega t)$$

$$= \epsilon_w \sigma_w \left[\left(\frac{\sigma_v}{\sigma_w} \sin \omega t + 1/2 \sin^2 \omega t \right) \cos \delta \right.$$

$$\left. + \left(1/2 \, \omega t - \frac{\sigma_v}{\sigma_w} \cos \omega t - 1/2 \sin \omega t \cos \omega t \right) \sin \delta \right] \Big|_{\omega t_1}^{\omega t_2} \tag{12}$$

For $\omega t_1 = 0$ and $\omega t_2 = 2\pi$ the area of the damping ellipse becomes:

$$A_Z = \pi \sigma_w \epsilon_w \sin \delta \tag{13}$$

For $\delta = \pi/2$ we have an ellipse whose axes are parallel to the coordinate axes, or a circle; in case σ_w is numerically equal to ϵ_w. For $\delta = 0$ the ellipse becomes a straight line.

The value of the integral of the denominator A_N is different for the different validity ranges given in Table 1.

Case 1 (Figure 2).—The prestress is greater than the alternating stress ($\sigma_v \geqq \sigma_w$).—This is the most frequent possibility in practice. In passing around the ellipse in the direction of the arrow—this corresponds to the course in the practical test—the product $\sigma \, d\epsilon$ has positive values between the points on the

TABLE I

REVIEW OF THE RELATIONS BETWEEN RELATIVE DAMPING D' AND PHASE
ANGLE δ OR PRESTRESS σ_v FOR THE PARTICULAR RANGES OF VALIDITY

$$\left(\text{WITH } \cos \alpha = \frac{|\sigma_v|}{\sigma_w} \right)$$

Range of validity	Relative damping
Case 1 (Figure 2):	
$|\sigma_v| \gtreqless \sigma_w$	$D' = \dfrac{\pi \sin \delta}{\dfrac{\pi}{2} \sin \delta + 2 \dfrac{|\sigma_v|}{\sigma_w}}$
Case 2 (Figure 3):	
$\sigma_w \gtreqless |\sigma_v| \gtreqless \sigma_w \cos \delta$ or $1 \gtreqless \cos \alpha \gtreqless \cos \delta$	$D' = \dfrac{\pi \sin \delta}{\left(\dfrac{\pi}{2} + \alpha \right) \sin \delta + (2 - \sin \alpha \sin \delta) \cos \delta}$
Case 3 (Figure 4):	
$\sigma_w \cos \delta \gtreqless |\sigma_v| \gtreqless 0$ or $\cos \delta \gtreqless \cos \alpha \gtreqless 0$	$D' = \dfrac{\pi \sin \delta}{\left(\dfrac{\pi}{2} + \delta \right) \sin \delta + (2 - \sin^2 \alpha) \cos \delta}$

ellipse A and C through B. The points A and C represent the angles $3/2\pi + \delta$ and $\pi/2 + \delta$. So we have:

$$A_N = \int_0^{\pi/2+\delta} \sigma \, d\epsilon + \int_{3\pi/2+\delta}^{2\pi} \sigma \, d\epsilon \tag{14}$$

and with Equation (12):

$$A_N = \sigma_w \epsilon_w \left(\frac{\pi}{2} \sin \delta + 2 \frac{\sigma_v}{\sigma_w} \right) \tag{15}$$
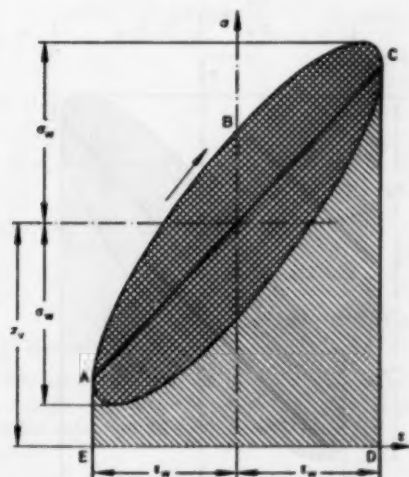
FIG. 2.—Damping ellipse for Case 1: $\sigma_v > \sigma_w$ and $\epsilon_p = 0$.
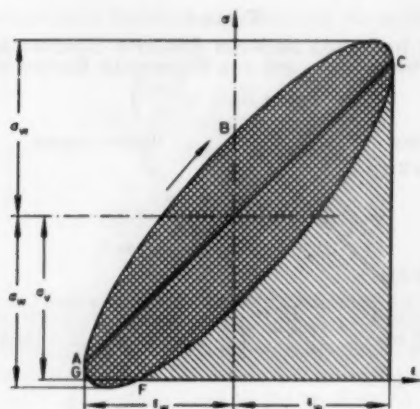
FIG. 3.—Damping ellipse for Case 2: $\sigma_w \cos \delta \leqq \sigma_v \leqq \sigma_w$.

and with Equation (13):

$$D' = \frac{A_Z}{A_N} = \frac{\pi \sin \delta}{\frac{\pi}{2} \sin \delta + 2 \frac{\sigma_v}{\sigma_w}} \tag{16}$$

Case 2 (Figure 3).The prestress lies in the range between σ_w and $\sigma_w \cos \delta$, $(\sigma_w \geqq \sigma_v \geqq \sigma_w \cos \delta).$—Here the damping ellipse dips below the ϵ axis. The sign of the work differential is now positive between A and B and between B and C and finally between F and G. Before we correlate angles with these points, for simplification we write:

$$\frac{\sigma_v}{\sigma_w} = \cos \alpha \tag{17}$$
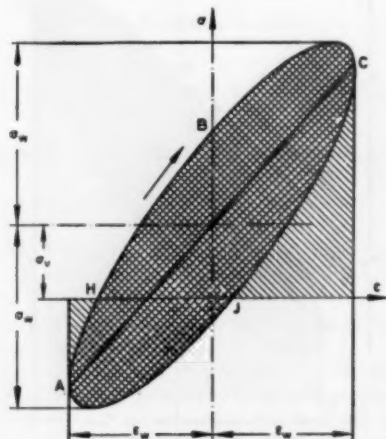
FIG. 4.—Damping ellipse for Case 3: $0 \leqq \sigma_v \leqq \sigma_w \cos \delta$.

and with Equation (8) we obtain

$$\sigma = \sigma_w \, (\cos \alpha + \sin \omega t) \tag{18}$$

We get the points of intersection, F and G, with the ϵ axis for $\sigma = 0$:

$$\sin (\omega t)_{1,2} = - \cos (\pm \alpha) = \sin \left(\frac{3\pi}{2} \pm \alpha \right) \tag{19}$$

Point F corresponds to the angle $3\pi/2 - \alpha$, the point G to the angle $3\pi/2 + \alpha$, point B to the angle δ or $2\pi + \delta$. Then we obtain Equation (20) for the value of A_N, and with Equation (12) we get Equation (21).

$$A_N = \int_{\delta}^{\pi/2+\delta} \sigma \, d\epsilon + \int_{3\pi/2-\alpha}^{3\pi/2+\alpha} \sigma \, d\epsilon + \int_{3\pi/2+\delta}^{2\pi+\delta} \sigma \, d\epsilon \tag{20}$$

$$A_N = \sigma_w \epsilon_w \left[\left(\frac{\pi}{2} + \alpha \right) \sin \delta + (2 - \sin \alpha \sin \delta) \cos \alpha \right] \tag{21}$$

and for the relative damping the result is:

$$D' = \frac{A_Z}{A_N} = \frac{\pi \sin \delta}{\left(\dfrac{\pi}{2} + \alpha \right) \sin \alpha + (2 - \sin \alpha \sin \delta) \cos \alpha} \tag{22}$$

Case 3 (Figure 4). The prestress is less than $\sigma_w \cos \delta$, $(0 \leqq \sigma_v \leqq \sigma_w \cos \delta)$. —We integrate here from B (δ or $2\pi + \delta$) to C ($\pi/2 + \delta$), from J ($3\pi/2 - \alpha$) to A ($3\pi/2 + \delta$), and from H ($3\pi/2 + \alpha$) to B. We get:

$$A_N = \int_{\delta}^{\pi/2+\delta} \sigma \, d\epsilon + \int_{3\pi/2-\alpha}^{3\pi/2+\delta} \sigma \, d\epsilon + \int_{3\pi/2+\alpha}^{2\pi+\delta} \sigma \, d\epsilon \tag{23}$$

and with Equation (12):

$$A_N = \sigma_w \epsilon_w \left[\left(\frac{\pi}{2} + \delta \right) \sin \delta + (2 - \sin^2 \alpha) \cos \delta \right] \tag{24}$$

For the relative damping we get:

$$D' = \frac{A_Z}{A_N} = \frac{\pi \sin \delta}{\left(\dfrac{\pi}{2} + \delta \right) \sin \delta + (2 - \sin^2 \alpha) \cos \delta} \tag{25}$$

The same expressions for A_N will be found for negative values of σ_v, based on grounds of symmetry. In all the equations, σ_v may be replaced by $|\sigma_v|$ and Equation (17) may be extended to Equation (26):

$$\frac{|\sigma_v|}{\sigma_w} = \cos \alpha \quad \text{or} \quad \alpha = \arccos \frac{|\sigma_v|}{\sigma_w} \tag{26}$$

The following conclusions can be drawn from the formulas of Table 1:

1. Relative damping D' is dependent on prestress. There are three ranges, depending upon the value of the ratio σ_v/σ_w, for each of which a particular expression for damping is valid (see Figures 2, 3 and 4).

2. The extent of each range depends in turn on the phase angle δ, at least so far as σ_v is smaller than σ_w.

3. At the limits of the respective ranges ($\sigma_v = \sigma_w$, $\sigma_v = \sigma_w \cos \delta$) the expressions for damping merge into each other.

4. D' agrees with the concept D given in the Standard, Equation (4) or (5), only in the particular case when $\sigma_v = \sigma_w$. Since the Standard is not confined strictly to this particular case, then D has a fictitious value when σ_v is different from σ_w which is difficult to evaluate; at any rate it does not agree with the values given in the concept section of the Standard.
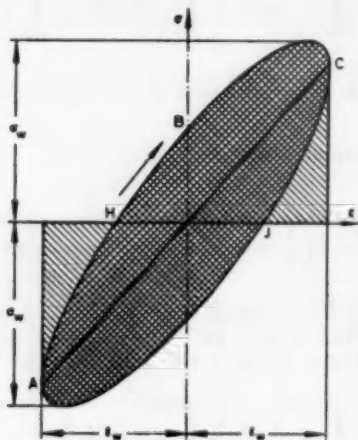
FIG. 5.—Damping ellipse for $\sigma_v = 0$ and $\epsilon_v = 0$.

Also, D' is illustrated geometrically. For example, when σ_v is greater than σ_w the denominator of the expression for D is represented by the area of the triangular figure FBAGF (Figure 1), but the denominator of the expression for D' is the area of the trapesoidal figure HFBAJH (Figure 1, see also the shaded area in Figure 2).

5. An important special case, which will be dealt with later, arises when $\sigma_v = 0$, Figure 5. In this case we have:

$$D' = \frac{\pi \sin \delta}{\left(\dfrac{\pi}{2} + \delta\right) \sin \delta + \cos \delta} = \frac{\pi}{\dfrac{\pi}{2} + \delta + \cot \delta} \tag{27}$$

If we make $\delta = \pi/2$ in the above equation, we have $D' = 1$, which means that the mechanical energy which is introduced is changed completely to heat. This is impossible as long as a prestress is present, and certainly as long as the force-displacement diagram is elliptical.

Although we started with a clear and intelligible verbal definition which uses

the energy principle, it is evident that we arrive at some unwieldy formulas. Now if we try to experimentally determine the dependence of the value of D' on prestress, we immediately find further difficulty (see Figure 13): the value of D' diminishes rapidly at higher prestresses. A certain amount of energy, so called "reactive energy", passes back and forth at the vibration frequency of the driver between the testpiece and the prestressing spring. This reactive energy is naturally included in the preceding calculations of D'. With high prestresses, this elastically-stored reactive energy finally grows large compared to the energy which is changed to heat. The dependence of the loss angle or of the damping D' upon the prestress is thus so covered up that it is no longer recognizable.
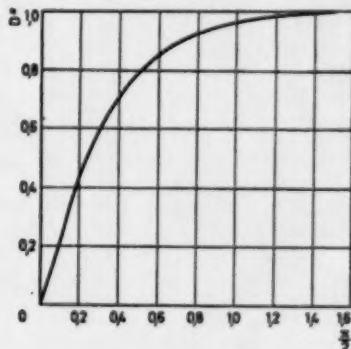
FIG. 6.—Dependence of the relative damping D'' on the phase angle δ from Equation (29).

This state of affairs makes it clear that we should abandon the verbal definition previously given and turn to the following:

Relative damping D'' = The portion of the energy which is changed to heat in each vibration cycle, divided by the mechanical energy furnished by the vibration driver for each cycle.

The differential for this expression is:

$dA = (\sigma - \sigma_v)d\epsilon$.   Equation (11) is then transformed to:

$$D'' = \frac{\int_0^{2\pi} (\sigma - \sigma_v)\, d\epsilon}{\int_0^{2\pi} f([\sigma - \sigma_v]\, d\epsilon)(\sigma - \sigma_v)\, d\epsilon} \tag{28}$$

It can be seen at once that the integration of Equation (28) leads to the same result as Equation (27) (prestress = 0, see also Figure 5), thus:

$$D'' = \frac{\pi}{\frac{\pi}{2} + \delta + \cot \delta} \tag{29}$$

TABLE II
COMPOUNDING RECIPES

	1	2	3
Smoked sheets	100.0	50.0	
Cold rubber (Polysar Krylene)		50.0	100.0
Zinc oxide, active	3.0	5.0	5.0
Stearic acid	3.0	1.5	1.5
Carbon black, ISAF	45.0	45.0	48.0
Naftolen ZD	4.5	5.0	4.0
Circosol 2XH			2.0
Cumarone resin		2.0	2.0
N-phenyl-N'-cyclohexyl-p-phenylenediamine (Antioxidant 4010)	1.0	1.0	1.0
Phenyl-1-naphthylamine (PAN)	1.5	1.0	1.0
Paraffin	0.6	0.6	1.0
Diphenylnitrosamine (Vulkalent A)	0.8		
N-cyclohexyl-benzothiazylsulfenamide (Vulkacit CZ)	0.45		1.3
N,N-diethyl benzothiazyl sulfenamide (Vulkacite AZ)		0.6	
Sulfur	2.5	2.0	1.75
Cure, min/° C	40/143°	40/151°	40/151°

	4	5	6
Butyl rubber (Polysar Butyl 301)	100.0		
Polychlorobutadiene (Perbunan C 210)		100.0	
Magnesia, usta leicht		3.0	
Poly(dimethyl siloxane) (Silopren)			100.0
4-Nitroso-N-methyl-N-nitrosoaniline	1.8		
Zinc oxide, active	0.5	5.0	
Pyrogenic silica			40.0
Benzoyl peroxide paste—(Silopren cross-linking agent BP 50)			2.5
Stearic acid	1.0		
Vaseline	3.0		
Naftolen ZD		5.0	
Carbon black, HMF	10.0		
Carbon black, CK3		35.0	
Mixed mercaptobenzothiazole + tetramethylthiuram disulfide (1:2) (Vulkacit MT/C)	1.5		
Aralkylated diphenylamine (Antioxidant DDA)		1.0	
Phenyl-1-naphthylamine (PAN)		1.0	
Sulfur	2.0		
Vulkacit NP		1.0	
Cure, min/° C	40/155°	25/151°	15/110° (Press) 15 hrs/200° (hot air)

TABLE II—(*Continued*)

	7	8	9
Smoked sheets	100.0		
Butadiene/acrylonitrile copolymer (Perbunan N 2810)			100.0
Zinc oxide, active	15.0		5.0
Zinc oxide, RS	30.0		
Carbon black, 101			30.0
Carbon black, CK3			8.0
Rosin			3.0
N-phenyl-N'-cyclohexyl-*p*-phenylenediamine (Antioxidant 4010)	0.75		
Phenyl-1-naphthylamine (PAN)	0.75		
Butyl ester of methylene-bis-thioglycolic acid (Plasticiser 88)			30.0
Dibenzothiazyl disulfide (Vulkacit DM)			1.2
Vulkacit 576	1.1		
Sulfur	3.0		1.8
Polyurethane rubber—ethylene glycol/adipic acid polyester-(Desmophen 2000) and 1,5-naphthalene diisocyanate (Desmodur 15).		100.0	
Cure, min/° C	40/133°		40/151°

Measured at +40° C and at another temperature near the maximum damping.

――――― (1) Natural rubber (tire compound).
―― ― (2) Blend of natural and synthetic (butadiene/styrene copolymer).
―― ― ― (3) Butadiene/styrene copolymer (Polysar-Krylene).
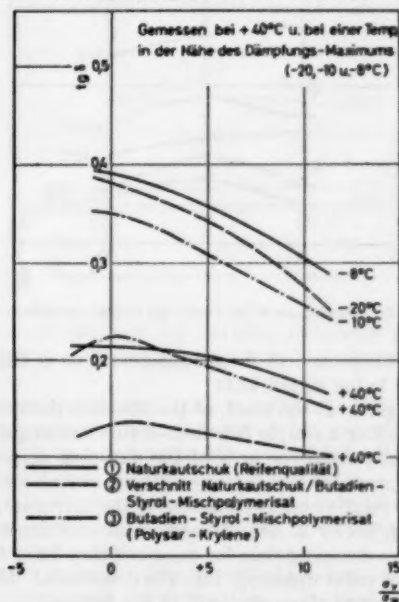
Fig. 7.—Dependence of loss factor tan δ upon the ratio σ_v/σ_w.

This is valid now for all values of prestress; the division into three ranges as in Table I disappears. Moreover, the prestress no longer appears in the equation.

The difference between D'' and D' is due to the fact that D' is derived using the total energy balance of the test specimen while the derivation of D'' uses the energy balance of the driver. In the latter case, the reactive energy drops out and its previously mentioned predominance does not appear.

D'' can be shown graphically as a function of δ and for each value of δ the corresponding value of the damping may be read from the graph, Figure 6. D'' lies between 0 and 1 or 0 and 100% for all prestresses.

Measured at +40° C and at another temperature near the maximum damping.
- ────── (4) Butyl rubber (Polysar-Butyl 301).
- ── ── (5) Polychlorobutadiene (Perbunan C210).
- ──── (6) Poly(dimethyl siloxane) (Silopren).

Gemessen bei +40°C u.bei einer Temp. in der Nähe des Dämpfungs-Maximums (-26,-2 u.0°C)

④ Butylkautschuk (Polysar-Butyl 301)
⑤ Polychlorbutadien (Perbunan C 210)
⑥ Polydimethylsiloxan (Silopren)
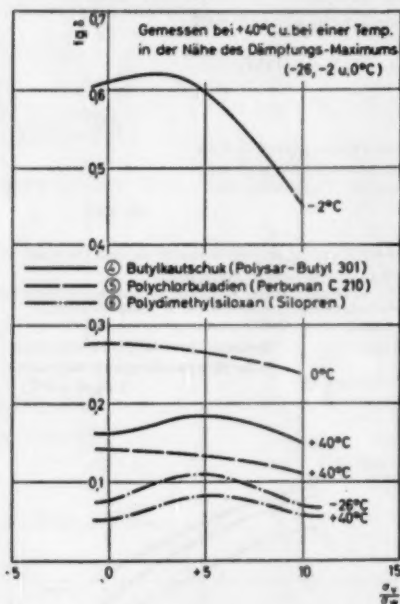
FIG. 8.—Dependence of loss factor tan δ upon the ratio σ_v/σ_v.

The practical consequence of these considerations is that two of the ideas presented are left as being significant:

1. The concept, given at the start, of the absolute damping in cal/cm³.

2. The loss angle δ or a simple function of this loss angle, be it sin δ (which can be derived directly from the area of the damping ellipse) or tan δ (this is the loss factor and provides the analogy with electrical oscillations) or finally D'' (which gives the relative energy balance of the driver in per cent).

The values given under 2. are dimensionless and are equivalent, to that extent, to the relative damping thus far used but they have the advantage that the prestress does not enter explicitly into the definition. Hence it is proposed to use one of the concepts given under 2. in the future.

EXPERIMENTAL

Without regard to the question of a suitable definition of damping, we have investigated the values of tan δ and of D'' in their dependence on prestress. The formulas for the vulcanizates which were used are given in Table II. Measurements were made with a damping apparatus which followed the principle of Roelig but which has been further developed in the meantime. It is now possible to read the phase angle directly from the apparatus without use of a

Measured at +40° C and at another temperature near the maximum damping.

> —————— (7) Natural rubber (cushioning compound).
> — — (8) Polyurethane rubber (Vulkollan 18 W).
> —— - —— (9) Butadiene/acrylonitrile copolymer.
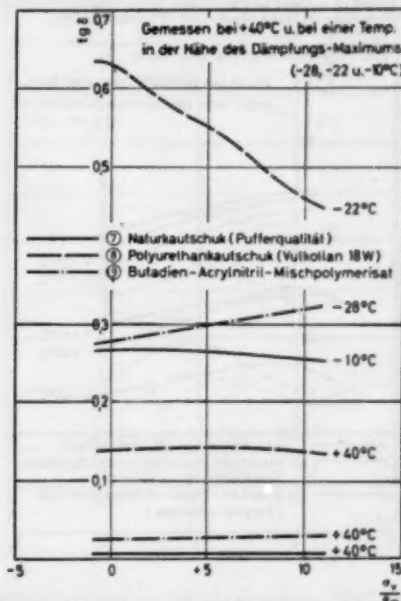
Fig. 9.—Dependence of loss factor tan δ upon the ratio σ_v/σ_w.

planimeter. Moreover, we can use smaller testpieces and more moderate forces. The present form of the apparatus and its characteristics will be described elsewhere.

Cylindrical testpieces were used, 1.1 cm in diameter and 1.8 cm long. Three pieces, each 0.6 cm long were stacked together for this purpose, because pieces of this thickness could be more uniformly vulcanized. The alternating stress σ_w amounted to 1.5 kg/cm², the frequency was 7.5 cps. The compression prestress σ_v was varied in multiples of σ_w up to ten times this value. In order to also include zero prestress and a point in the extension range, the testpieces were adhered to the metal plates.

Figures 7, 8, and 9 show the dependence of the loss factor tan δ on the prestress, or, more accurately on the ratio σ_v/σ_w. Each of the nine types of vul-

canizates was measured at two different temperatures: at $+40°$ C and then at another temperature, naturally different for each vulcanizate, which was near the maximum damping. The temperature of maximum damping itself was not chosen because the accuracy of measurement was low at that point. At that particular temperature the testpiece is so hard that the flexure of the dynamometer with respect to the deformation of the sample cannot be neglected. For the same reason the values at even $10°$ C above the maximum must be corrected, but the correction here is so small that the precision of measurement is very slightly affected.

Measured at $+40°$ C and at another temperature near the maximum damping.

———— (1) Natural rubber (tire compound).
— — — (2) Blend of natural and synthetic (butadiene/styrene copolymer).
—·—·— (3) Butadiene/styrene copolymer (Polysar-Krylene).

Gemessen bei +40°C u.bei einer Temp. in der Nähe des Dämpfungs-Maximums (-20,-10 u.-8°C)

-8°C
-20°C
-10°C
+40°C
+40°C
+40°C

① Naturkautschuk (Reifenqualität)
② Verschnitt Naturkautschuk/Butadien-Styrol-Mischpolymerisat
③ Butadien-Styrol-Mischpolymerisat (Polysar-Krylene)

$\frac{\sigma_v}{\sigma_w}$
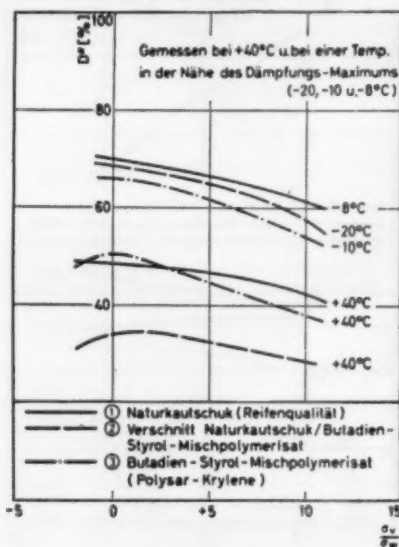
FIG. 10.—Dependence of relative damping D'' on the ratio σ_v/σ_w.

The testpieces were maintained for half an hour at the desired temperature before the measurements were made. Every piece was then measured six times at the constant temperature, each time passing from low to high prestress values, and then back again. The whole test for each piece required about two hours. This method was necessary in order to be sure that the testpiece under the periodic loading would be in temperature equilibrium with the surroundings.

In the case of a tire compound of natural rubber (Recipe 1), the dependence of the loss factor on prestress was quite small at $+40°$ C, but was greater at $-8°$ C. In the latter case tan δ fell relatively rapidly with increasing prestress.

A tire compound (Recipe 2), made from a blend of natural rubber and cold rubber showed a weakly defined maximum at about $\sigma_v/\sigma_w = 0$ in the tests at $+40°$ C. The same type of maximum was also shown in the same range by a

cold rubber tire compound (Recipe 3).   Both these compounds showed a reduction in tan δ with increasing prestress at the lower temperatures ($-20°$ C and $-10°$ C).

A butyl rubber vulcanizate (Recipe 4), when measured at $+40°$ C, showed a maximum when the value of σ_v/σ_w was about 5.   At $-2°$ C, tan δ ran through a slight maximum and then fell sharply as the prestress increased.

A polychloroprene vulcanizate (Recipe 5) showed only a weak dependence of the loss factor on prestress at both $0°$ and $40°$ C.

Measured at $+40°$ C and at another temperature near the maximum damping.

——— (4) Butyl rubber (Polysar-Butyl 301).
— — (5) Polychlorobutadiene (Perbunan C210).
— – — (6) Poly(dimethyl siloxane) (Silopren).
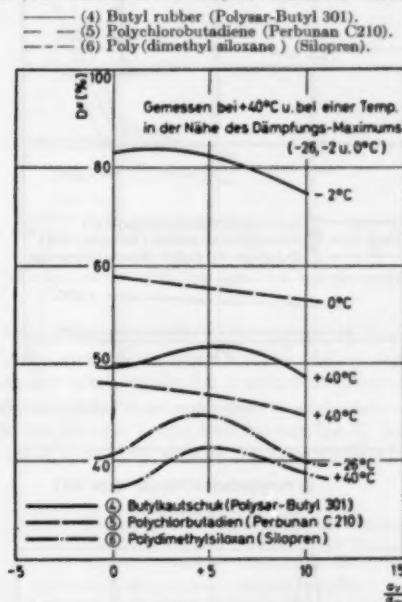
FIG. 11.—Dependence of relative damping D'' on the ratio σ_v/σ_w.

A vulcanizate based on poly (dimethyl siloxane) (Recipe 6) was measured at $-26°$ and at $+40°$ C.   The curves lie relatively close together (slight temperature dependence of the properties of silicone rubbers!).   There was a maximum at a σ_v/σ_w value of 5 to 5.5 for both curves.

A natural rubber cushioning compound (Recipe 7) had about the same loss factor for all the values of prestress used.   This was true both at $-10°$ C and at $+40°$ C.

A polyurethane rubber (Recipe 8) had a loss factor at $-22°$ C which dropped rapidly with increasing prestress.   At $+40°$ C the loss factor was almost constant.

An oil resistant vulcanizate (Perbunan N 2810, Recipe 9) was unique in the whole series of vulcanizates in the fact that it showed an increasing loss factor with rising prestress in tests at $-28°$ C.   On the other hand, at $+40°$ C, practically no dependence of the loss factor on prestress was noted.

Figures 10, 11, and 12 give the values of the relative damping D'' calculated

Measured at $+40°$ C and at another temperature near the maximum damping.

    —————— (7) Natural rubber (cushioning compound).

    — — — (8) Polyurethane rubber (Vulkollan 18 W).

    – — – — (9) Butadiene/acrylonitrile copolymer.
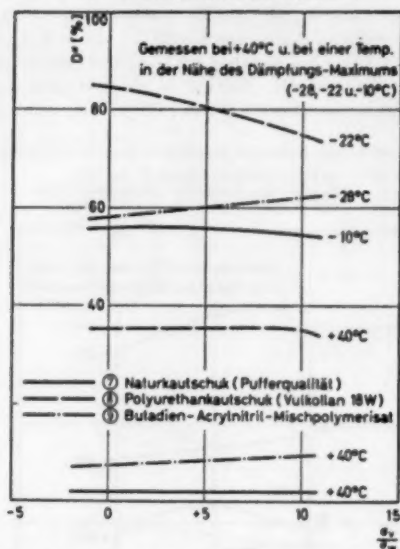
Fig. 12.—Dependence of relative damping D'' on the ratio σ_v/σ_w.
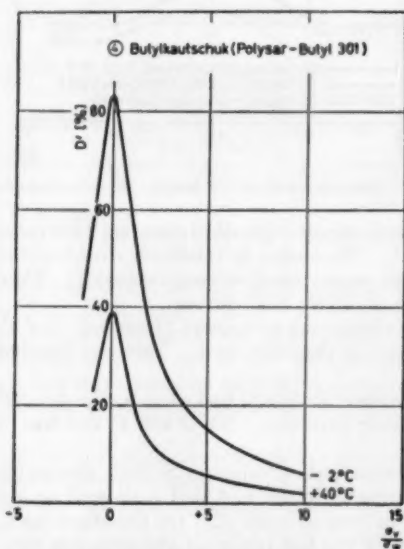
Fig. 13.—Dependence of relative damping D' on the ratio σ_v/σ_w.
(4) Butyl rubber (Polysar-Butyl 301).

——— (1) Natural rubber (tire compound).
— — (2) Blend of natural and synthetic (butadiene/styrene copolymer).
—·— (3) Butadiene/styrene copolymer (Polysar-Krylene).
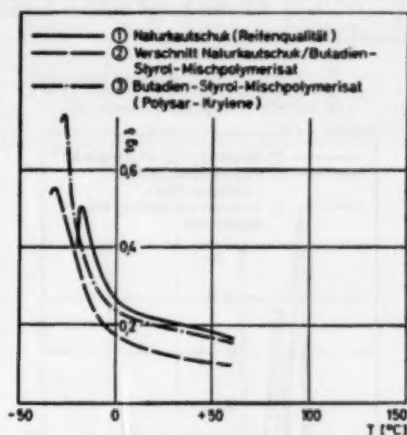
FIG. 14.—Dependence of the loss factor tan δ on the temperature.

from these same measurements of δ. The course of the curves is about the same; they seem to be somewhat more leveled out at higher damping values compared with those for tan δ, while the maxima at lower damping values seem somewhat more pronounced.

Figure 13 gives, for Recipe 4, the two curves for D' which were calculated with the same values of δ as were used in Figures 8 and 11. A sharply defined

——— (4) Butyl rubber (Polysar-Butyl 301).
— — (5) Polychlorobutadiene (Perbunan C310).
—·— (6) Poly(dimethyl siloxane) (Silopren).
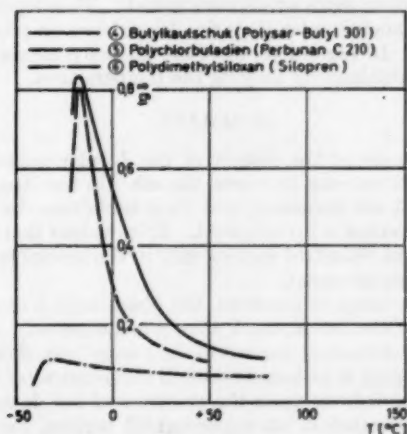
FIG. 15.—Dependence of the loss factor tan δ on the temperature.

maximum is shown here for $\sigma_v/\sigma_w = 0$ and this appears for all the vulcanizates when D' is plotted against σ_v/σ_w. The characteristic maximum shown in Figures 8 and 11 at $\sigma_v/\sigma_w = 5$, for the butyl rubber is entirely repressed in Figure 13 by this type of plotting.

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——— (7) Natural rubber (cushioning compound).
— — (8) Polyurethane rubber (Vulkollan 18 W).
— · — (9) Butadiene/acrylonitrile copolymer.
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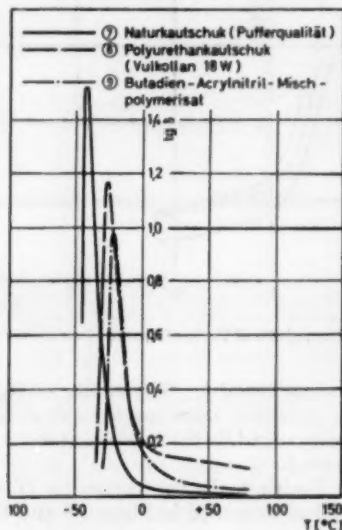

FIG. 16.—Dependence of the loss factor tan δ on the temperature.

Figures 14, 15 and 16 show the dependence on temperature of the loss factors for all nine of the vulcanizates which were tested. This dependence on temperature is seen to be much greater than the dependence on prestress as shown in Figures 7, 8 and 9. In particular, there are no sharp maxima in the prestress curves such as are obtained by varying the temperatures.

SUMMARY

After a short review of the history of the development of the concept of damping, the definitions—one in words, the other in the form of an equation—given in DIN 53513 are discussed, and their usefulness for measurements at various values of prestress is investigated. It is evident that the mathematical definition given in the Standard applies only in the special case when prestress and alternating stress are equal.

For the complete range of prestress, the phase angle δ or some simple function of δ, such as the loss factor, tan δ, should be measured. If it is desired not to relinquish the percentage statement of the energy loss, then a new definition for the relative damping is proposed which is independent of the prestress, just as is tan δ. The dependence upon the prestress of the damping values under discussion is demonstrated in an experimental section, for various types of elastomers.

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THE ROLLING RESISTANCE OF A WHEEL
WITH A SOLID RUBBER TIRE *

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In a paper on the mechanism of rolling friction Tabor[1] suggests that rolling friction in the elastic range is primarily due to elastic hysteresis losses. Independently of Tabor, though subsequent to his work on the subject, the author had used the same postulate to calculate the rolling resistance of a wheel with a solid rubber tire.

THEORY

The problem is regarded as one in plane strain, the wheel being considered as a long composite cylinder consisting of a rigid core of radius a and a perfectly elastic deformable tire of external radius b and width s. When the wheel is loaded by a weight W and itself bears on a rigid horizontal plane there is a zone of contact in which the pressure will increase from zero at the edges to a maximum along the center line. Ideally, we should like to know the form of this pressure distribution and the distortion of the tire produced by it, but there appears to be no tractable analytic solution of this problem. Accordingly the problem of the work done in deforming the tire is tackled indirectly by making some rather sweeping assumptions, the merit of which must be judged from a comparison of the answer they give with experiment.

In the first place we assume that if p_0 is the average contact pressure and u the maximum vertical compression of the tire, the work done in compressing unit area of the tire through a distance u as the wheel turns is $p_0 u$. If, owing to the resilience of the tire, the work is recovered except for a fraction h we may write

$$\text{Work dissipated by wheel per revolution} = h p_0 s u \cdot 2\pi b \qquad (1)$$

If v is the velocity of the driving vehicle, the number of revolutions per unit time is $v/2\pi b$, hence the rate of working per wheel is $h v p_0 s u$, and the rolling resistance is defined by the expression

$$R = h p_0 s u \qquad (2)$$

Let the flattened zone of contact between tire and plane have breadth e; then, if the distortion of the neighboring portions of the tire can be neglected, $e^2 \simeq 8bu$, and

$$p_0 = W/2s(2bu)^{\frac{1}{2}} \qquad (3)$$

Equations (2) and (3) contain three unknowns, R, p_0 and u, so that we need a further relation between p_0 and u to solve for R. The assumption made is that in the narrow zone of contact between tire and plane the elastic stresses

are the same as if the whole surface of the tire were acted upon by an external uniform normal stress p_0. This enables us to obtain a relation between p_0 and u by means of Lamé's well-known solution for the elastic stresses in a hollow cylinder submitted to external and internal pressures[2]. If these are p_0 and p_i respectively, we have the following solution for the stresses at a radius r:

$$\sigma_r = (A/r^2) + 2C$$
$$\sigma_\theta = -(A/r^2) + 2C \tag{4}$$

where

$$A = \frac{a^2 b^2 (p_0 - p_i)}{b^2 - a^2}, \quad 2C = \frac{p_i a^2 - p_0 b^2}{b^2 - a^2}$$

The general expressions in polar co-ordinates for the displacements relating to a symmetrical stress distribution in a cylinder are[2]

$$u = \frac{1}{E}\left[-\frac{(1 + \nu)A}{r} + 2C(1 - \nu)r \right] + H \sin\theta + K \cos\theta$$
$$v = Fr + H \cos\theta - K \sin\theta \tag{5}$$

where u is the radial and v the tangential displacement. E is Young's modulus for the tire material and ν Poisson's ratio. A and C are defined by Equations (4), and F, H and K are determined by the boundary conditions. Since the displacements are independent of θ, $H = K = 0$. Also, in this application of the theory there is a rigid core in place of the hollow of Lamé's solution so that $u = v = 0$ at $r = a$. Hence $F = 0$, so that the tangential displacement is everywhere zero, and also

$$0 = \frac{1}{E}\left[-\frac{(1 + \nu)A}{a} + 2C(1 - \nu)a \right] \tag{6}$$

Equation (6) can be solved for p_i, giving

$$p_i = 2p_0 b^2 / [a^2 + b^2 + \nu(b^2 - a^2)]$$

For rubber we may put $\nu = \frac{1}{2}$ and therefore

$$p_i = 4p_0 b^2 / (a^2 + 3b^2) \tag{7}$$

This value is substituted in Equation (5), giving for $r = b$,

$$Eu = -\frac{3}{2} p_0 (b - a)\left(\frac{ab + b^2}{a^2 + 3b^2}\right) \tag{8}$$

The negative sign enters because u is a compression, and no ambiguity will arise if it is omitted. Further, for a thin tire on a large wheel, a and b are very nearly equal and $(b - a)$ is the tire thickness t. Equation (8) may therefore be written

$$Eu = \frac{3}{4} p_0 t \tag{9}$$

Eliminating p_0 and u between Equations (2), (3) and (9),

$$R = (h/4.4)\,(W^4 t / E s b^2)^{\frac{1}{4}} \tag{10}$$
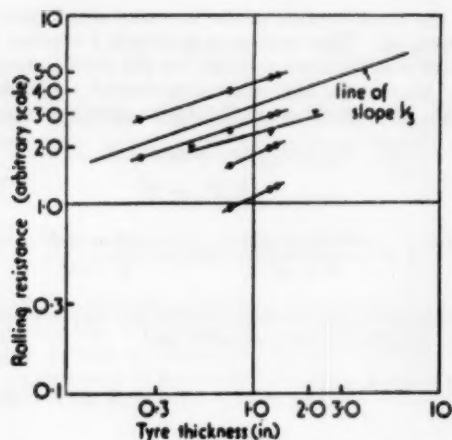
FIG. 1.—Variation of rolling resistance with tire thickness.

EXPERIMENTAL RESULTS

A perusal of available records in which R was measured on a tire-testing machine shows that the proportionality of rolling resistance to the cube root of tire thickness is closely borne out (Figure 1). Further, elimination of p_0 between Equations (3) and (9) gives a relation between load and compression which should be applicable to static loading tests:

$$W = (8Es/3t)(2bu^3)^{\frac{1}{3}} \qquad (11)$$
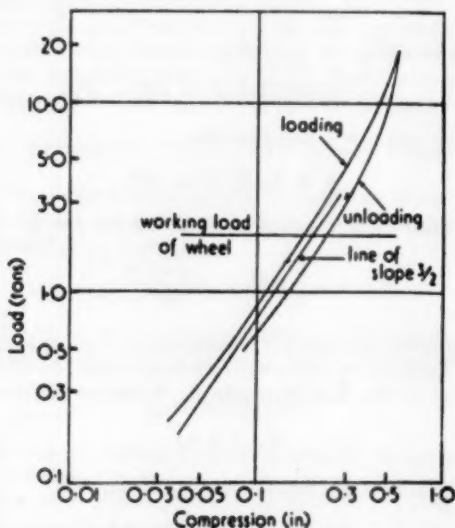
FIG. 2.—Static load-compression test for wheel.   Dimensions of wheel: diameter of rigid core =27.4 in.; tire thickness =2.16 in.; tire width =4.75 in.

Here, again, the prediction that the slope of the line showing log W against log u should be $3/2$ is very well corroborated over the range of load which is relevant to practice (Figure 2).

As regards verification of Equation (10) as a whole, experimental data for comparison were obtained from a tire-testing rig in which a loaded wheel is driven by a drum of large diameter controlled by a d.c. motor, the power input to the motor being measured. Similar wheels of 30 in. diameter with three different thicknesses, 2.16 in., 1.26 in. and 0.47 in. were tested at two loads, 40 cwt and $71\frac{1}{2}$ cwt, and at equivalent driving speeds of 10, 15, 20, 25 and 30 m.p.h. The tests can be regarded as only very rough since the rig is used normally for routine testing and is far from satisfactory for research purposes. The effective value of E, deduced from the compression test of Figure 2 by means of Equation (11), is 1900 lb/in.^{2}. Unfortunately, during the test (which had been carried out for another purpose), no hysteresis loops had been traced relating to the loadings used in the rolling tests, and for the value of h it has been necessary to accept the manufacturers' quotation of 0.2, measured by the Dunlop pendulum.

TABLE I

COMPARISON OF OBSERVED AND CALCULATED VALUES
OF ROLLING RESISTANCE

Load (cwt)	Tire thickness (in.)	Rolling resistance (lb)	
		Observed	Calculated
40	2.16	38.2	34.8
	1.26	30.1	29.1
	0.47	25.1	21.0
$71\frac{1}{2}$	2.16	80.6	75.8
	1.26	54.4	63.3
	0.47	44.1	45.5

It can be seen from the table that observed and calculated values are roughly in agreement. That may be partly fortuitous, owing to uncertainty in the value of h. However, in view of the other evidence presented, and especially also in view of Tabor's validation of the fundamental physical assumption, it is possible to suggest that Equation (10) does give a reasonably accurate value for rolling resistance.

SUMMARY

The rolling resistance of a wheel with a solid rubber tire, running on a rigid plane surface, is calculated on the assumption that it is due to hysteresis losses in cyclic deformation of the rubber. The results and certain other deductions from the theory are in reasonably good agreement with experimental observations.

ACKNOWLEDGMENT

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THE STATUS OF THE THEORY OF BOND
STRENGTH IN MULTIPLY ARTICLES *

G. L. Slonimskiĭ

The task set before me by the Organizing Committee of this Conference is to attempt a systematic consideration of the principal theoretical aspects of the numerous articles relating to the problem of bond strength between the elements of multiply articles. It is natural that a report of this kind can be neither an exhaustive survey of all the theoretical ideas in this field, nor a generalization of published or original experimental data. The former was not possible on account of the exceptional complexity of the problem, touching on a wide circle of questions of technology (formulation and processing) physics, chemistry, theoretical mechanics and other disciplines; the latter is the subject of special reports.

In recent years a large number of investigations have been carried out, giving valuable results on the theory of bond strength and making possible successful solutions of a number of practical tasks.

Here we must in the first place recall the investments carried out in the NIIShP (Tire Research Institute) on bond strength between elements of motor tire casings, by large teams of workers under the direction of G. N. Buĭko, V. A. Pinegin, B. A. Dogadkin, M. A. Tsydzik and S. L. Levin. As a result of these studies data were obtained on the influence of formulation, technological, physical chemical and structural factors upon bond strength, and methods of testing multiply specimens and tires for ply separation worked out.

A series of interesting studies was carried out also in the laboratories of the Yaroslavl and Moscow tire works.

The studies, containing a large amount of experimental and theoretical material, gave rise to a lively demand for the exchange of data and the assessment of theoretical questions, for which, e.g., the present conference was convened.

In the development of theoretical ideas in the field of bond strength between elements of multiply articles fundamental importance attaches to the studies by P. A. Rebinder and his coworkers, dealing with physical chemical investigations of surface properties, and also to the work of B. V. Deryagin and his coworkers, dealing with questions of interaction of surfaces.

Nevertheless in spite of certain successes there is still no theory which makes it possible to determine one's position in the problem of ply separation in tires of synthetic rubbers or to develop general and adequately effective methods of combating ply separation. It must be observed that even a successful solution of this problem for the various types of tires, prepared from given materials, does not reduce the pressing nature of the problem, since it is inevitable that there will appear in due course new types of synthetic rubbers and cord materials, alterations in dimensions and structural parameters of the tires, which may involve new forms of ply separation. Consequently it is necessary to

obtain a fundamental solution of the problem of ply separation, i.e., to describe the mechanism of ply separation and the dependence of this phenomenon upon the properties of materials, the methods of production of the tires, the structural parameters and so on. Only a knowledge of the basic laws underlying the process of ply separation will make it possible to develop general methods for combating this form of tire destruction.

Production and service of tires introduces two principal problems calling for investigation and solution. First, this is a problem of the tackiness of the raw stocks, since in the process of building casings (and inner tubes) it becomes necessary to join together the separate elements of the article. The bond strength in this case must be effected by the tackiness of the contacting elements of the casing. In the second place, this is a problem of the bond strength between the elements of the finished article, since it is necessary for the tire to be maintained in a complete form in the process of service, during which it is subjected to repeated and complex deformations. In this case the bond strength must be effected by attachment between the elements of the tire, taking place during vulcanization of the covers, and to a certain extent altering in the service of the tires as the result of the inevitable development of the fatigue process, and also of other forms of aging. We will restrict ourselves to a consideration of the second question and will not analyze the problem of tackiness.

It is quite evident that the subject of the theoretical investigation must be the joint, i.e., we must solve the following questions: What is the joint, what are its characteristics, and how is it destroyed.

On joining two materials of different or similar nature two different types of joint are possible. Thus, for instance between the surface of the fibers, forming the cord thread, and the rubber attaching to it, there must be maintained a sharp interface, while in plying up of two vulcanized rubbers the maintenance of such a boundary is possible but not obligatory. The boundary between two vulcanized rubbers may be sharp or diffuse to a certain degree (depending upon the properties of the vulcanization stocks, the conditions of building and vulcanization), while in the case of plying up of identical rubbers it may even disappear entirely.

Thus three types of joint are possible: one maintaining the interface, one with the formation of a transitional boundary layer, and one with complete disappearance of nonuniformity in the boundary range. Consequently in theoretical investigation we must use contemporary ideas about adhesion, and also about cohesion.

If we turn to actual data, we are immediately struck by the dependence of the phenomena of ply separation of a multiply article upon a combination of many interacting factors; not one of these can by itself be considered as the main one, entirely determining the course of the phenomenon, and not one of them can be investigated independently of the others.

From this there follows the primary necessity of determining the internal relation between the factors which influence ply separation. Only along this line must we seek a guiding idea by which we can find our way in the huge amount of factual material and understand the role and importance of each factor in whatever are the concrete conditions of operation of the tire.

One characteristic peculiarity of ply separation of casings is that it takes place after a considerable number of deformations. Casings which undergo ply separation immediately or after a small number of cycles of deformation, are regarded as rejects. Thus interest attaches to the case where ply separation

occurs not immediately but after some time from the beginning of service of the casing.

From this it follows that ply separation is the result of development of the process of fatigue of the boundary layer. In fact if the articles or the specimen withstand one cycle of deformation they must be subjected to as many cycles as is desired if the properties of the material do not alter after each cycle. Consequently ply separation after many cycles of deformation is evidence of the taking place of a process of alteration of the material, which leads in the last resort to destruction of the joint. Such a process of alteration of the material under repeated mechanical action is nothing other than fatigue of the material. If the article were uniform both in the property of the material from which it was made and in the nature of the distribution of the forces in it, then destruction might begin at any point. Ply separation at the joint shows that in such cases fatigue of the joint, i.e., of the boundary layer, for some reason has developed more rapidly than the fatigue of the other parts of the article.

Thus to explain the mechanism of ply separation of multiply articles it is necessary to determine the influence of a whole combination of factors upon the process of fatigue of the polymer (vulcanized rubber, cord) and upon the peculiarity of the boundary layer.

The process of fatigue of vulcanized rubbers and other polymeric materials have in recent years been the subject of detailed study. At the present moment theoretical ideas of the nature of this process have been developed[1].

The process of fatigue of a polymeric material begins with the formation of free radicals as the result of the mechanical scission of the chain molecules during deformation. The free radical formed in the material determines the development of secondary chemical processes, which proceed according to the chemical peculiarities of the actual material, having as a result an alteration in the properties of the material, and in particular of the elasticity and the strength.

The particular feature of the secondary chemical processes is their auto-acceleration and their high sensitivity to the amount of free radicals, formed as a result of deformation. Therefore the process of fatigue takes place in a non-identical way for different routines of mechanical action (since with an alteration in the routine there also changes the amount of free radicals formed per unit of time). In those parts of the article where the conditions of action are particularly heavy or the strength of the original material is reduced for some reason, there develops a more profound process of alteration of the material, leading to the formation of micro defects, while the remaining part of the material alters to a considerably less extent. The growth of the micro defect during subsequent deformations leads to the final destruction of the article.

Thus the fatigue of a given article develops in accordance with the chemical reaction capacity of the material from which it is made, and depends greatly upon the conditions under which the article is operating (mechanical and temperature conditions).

Since our task is to consider the process of ply separation, we are limiting ourselves to the above general ideas of the mechanism of the fatigue, and will pass to an analysis of the peculiar nature of the fatigue, which develops in the joint region of two polymers of different nature, i.e., the particular nature of the fatigue of the boundary layer.

The peculiar nature of the fatigue of the boundary layer must be determined by the conditions of formation of this layer, which obviously differ from the conditions of formation of the uniform parts of the article, and also difference

of the routine of deformation in the joint region from the routine of deformation in the uniform regions.

Formation of the boundary layer.—The formation of the boundary layer in the plying up of two materials of the same nature begins with the uniting of the surfaces of two bodies. This must ensure a close contact between the surfaces and may be achieved in the case of two vulcanizing stocks (or in the case of vulcanizing stock and cord) either by spreading, or by elastic deformation. In the latter case a firm contact is achieved by deformation of the surface irregularities, as a result of which stresses are always formed at the boundary. Consequently it is necessary to aim for conditions of plying up in which as it were one of the materials being joined together is capable of significant viscous flow.

It is from this very point that there emerges the essential role of flowability and elasticity of the raw stocks, i.e., the so called viscoelastic properties. Since the flowability and elasticity of a given polymer are determined by the chemical composition, the structure and the length of the chain molecules, interacting with the filler, the degree of mastication and other physical chemical factors, there is no doubt of the essential roles of the physical chemical characteristics of the raw rubbers and raw stocks in the analysis of the phenomenon of ply separation.

On the other hand it is evident that the dependence of the flowability and elasticity upon the composition of the mix is directly connected with the influence of the formulation factors upon the phenomena of ply separation which arise even in the first stage of joining the surfaces during their contacting. It is from this same point that there follows the great part played by such technological factors as the temperature and the pressure at which the plying up is carried out, and also the duration of the plying up. The influence of all the stated factors becomes evident at the different stages of formation of the boundary layer and is well-known from practical experience. These factors determine the quality of the contact between the surfaces, and consequently the presence or absence in the boundary layer of stresses and defects, and also the degree of interpenetration of the contacting materials.

The use of bonding agents together with other tasks serves the same purpose—the production of the fullest possible contact between the surfaces by introducing between them a very mobile bonding layer.

In addition to the actual process of contacting of the two layers, a no less important part is played by the constitution of the surfaces being joined. No demonstration is necessary to show that the surface of the raw vulcanizing stocks is highly variable. It is capable of oxidation in a greater degree than the deeper part of the material, since it is in immediate contact with the air; it may become dusty on storing before plying up; it is easy for the highly volatile substances in the surface part of the raw stock to be released from it; on the surface there are separated (blooming) the different compounding ingredients added to the stocks in excess of the correct amount (greater than can go into solution); finally the thermal motion of the flexible chain molecules on the surface of the material may differ from the movement within the material, as a result of which the properties of the fresh surface are bound to alter with time.

Consequently to understand the phenomenon of ply separation it is necessary to take into account the variability of the surfaces, depending upon the factors of the mix formulation, technology, and physical chemical factors.

A deliberate alteration in the condition of the surface is widely used in the

production of multiply articles (the use of impregnants, bonding agents, freshening-up or buffing of the surface and so on).

In addition to the variability of the surface layer of the raw vulcanizing stocks before plying up, it is necessary to take into account the variability of the contacting surfaces of the layers at the time of plying up and all the subsequent processes, leading to the formation of the vulcanizate. Here above all there is possible a mutual solution of the raw rubbers, which, as a result of their high viscosity, can take place only in the boundary layer, and also a redistribution of the soluble ingredients, which are capable of diffusing out of one layer into another.

These phenomena undoubtedly take place and have led technologists to agree on the formula of plying up stocks. However as yet there is no systematic physical chemical investigation of all the complex of questions which arises here, although individual points (the mutual solubility of rubbers, the vulcanization of bonding layers) have already been studied. There must also arise in the boundary layer a considerable alteration in the composition of the stocks, and consequently in the properties of the vulcanized rubber.

It is quite clear that the fatigue of the boundary layer must be different from the fatigue of the rest of the material for all the reasons given above:

(a) as a result of the alteration of the condition of the surfaces during preparation for plying up;

(b) as a result of the formation at the boundary of the pliedup layers of stresses and defects, depending upon the conditions of contacting;

(c) as a result of the alteration in the composition of the boundary layer in the process of plying up, and as a result of the alterations caused by this in the properties of the vulcanizate in the boundary layer.

The formulation, technological and physical chemical factors do not show one definite influence upon the bond strength, but cause this or that action depending on whether they take place during contacting, storage or vulcanization. In addition their considerable mutual influence occurs in a very evident form. For example we may indicate that the redistribution of the compounding ingredients in the boundary layer depends upon the formula, but the degree of redistribution which occurs in actual fact is determined by the capacity for diffusion. The diffusion itself, in the first place, depends upon the values of the coefficient of the diffusion of the ingredients in the mix in question and upon the external parameters of the process (temperature and duration). The degree of redistribution of the compounding ingredients achieved determines the course of the process of vulcanization, and consequently also the physical-mechanical properties of the vulcanizate in the boundary layer.

This example once again shows the cause of the lack of the success of the investigations carried out hitherto, in which an attempt was made to isolate a single basic factor which directly influenced the bond strength. There is no such factor. Only by revealing the internal connection between a group of factors which determine the properties of the boundary layer, in the first place its capacity for fatigue, can we understand the phenomenon of ply separation.

In conclusion it is necessary to consider the question of the nature of the bond between two bodies of different nature. As already indicated, in the plying up of two vulcanizing stocks it is possible to have formation both of a clear boundary between them and of a transitional layer. In the latter case the phenomenon more or less acquires a cohesion character. As a result of the lack of data about the transitional layers we must express a wish for this question to be studied, and for the present we must limit ourselves to con-

siderations of the case where two surfaces are maintained, forming a clear boundary.

In joining two surfaces there arise forces of attraction, governed by intermolecular, chemical and electrical interactions. B. V. Deryagin in his theory of adhesion[2,3] shows that the work of stripping of a film from a surface to which it is applied amounts to 10^4–10^6 erg/cm^2, while the surface tension even of a diamond is considerably lower (for solid bodies it is 10^2–10^4 erg/cm^2). From the fact that the surface tension gives a work of formation of 1 sq. cm of surface it follows that neither the intermolecular nor the chemical forces can be sufficient to effect such high values of the work of stripping. On the basis of these and other considerations, true only in the case where the stripping is not accompanied by deformations of the material and where the area of the surfaces formed is determined correctly, B. V. Deryagin draws the conclusion of the decisive role of the electrical forces in adhesion (the electrical forces arise as a result of the formation at the boundary of the two dielectrics of a double electral layer). Tearing takes place along the double electric layer, and whatever the strength is determines the electrical properties of the surfaces.

The main results of the theory of adhesion, advanced by B. V. Deryagin, must be borne in mind in studying the phenomenon of stripping. Nevertheless this theory does not take into account a series of moments, which are extremely important in the case of ply separation of polymeric systems.

In the first place, as already pointed out, it is possible to have the formation of a transitional layer, as a result of which the ply separation loses the character of the phenomenon of adhesion and acquires a cohesion character. Since this layer may have a very small magnitude, there is the possibility of a transitional character of phenomenon, which makes the physical picture extremely complicated. This peculiarity must be clearly expressed with polymers, as a result of the chain structure of their molecules and the flexibility which belongs to such molecules.

A second peculiarity is the occurrence of ply separation only after a large number of deformations. From this it follows that if the resistance of vulcanized rubbers to ply separations were in fact governed only by the electrical forces in the double electric layer, then these forces ought to alter with repeated deformations. Nevertheless the theory of adhesion of B. V. Deryagin does not give an explanation of the variability of the electrical double layer during repeated deformations.

Thus the electrical theory of adhesion cannot be applied to the phenomenon of ply separation of multiply polymeric articles.

Conditions of deformation of the boundary layer.—The condition of deformation in the joint zone do not coincide with the conditions of deformation of the whole specimen or of the article as an entirety. It is well known that under conditions of identical external action (for instance, under a repeated shear of a compressed specimen) ply separation has a completely different character and sets in in markedly different times as a function of the arrangement of the joint relative to the plane of shear (with identical dimensions and construction of a cubical specimen). Consequently in consideration of the problem of bond strength between elements of a multiply article it is necessary to devote particular attention to the question of the construction of this article. This is important not only from the point of view of finding the principles of construction which have the greatest resistance to ply separation, but also from the point of view of developing laboratory methods of assessing bond strength, which make it possible to assess this strength in service conditions.

The part played by the pattern of deformation of a joint is determined by the high sensitivity of the process of fatigue to the pattern of action of forces upon polymer. This sensitivity is a consequence, as has already been pointed out, of the dependence of the amount of free radicals formed upon the condition of deformation, and also of the dependence of the rate of growth of the existing or arising deformations of defects upon the conditions of deformation.

The difference in pattern of deformation of a joint from the pattern of deformation of uniform bodies is a consequence of the difference of the elastic constants of the pliedup materials and also of the boundary layer itself, if it has a finite thickness. The presence of internal surfaces, on which the elastic properties change sharply, leads to alteration in the character of the stresses and of the deformations in the whole specimen, but in a number of cases these alterations are localized close to the joint.

As an example let us consider the uni-axial compression of the cylinder, consisting of two identical cylinders, made from specimens and soft rubber (see Figure 1). In this case the stopper, which is compressed without lateral expansion (Poisson's coefficient close to zero), and the rubber, which is compressed while maintaining its volume (Poisson's coefficient close to 0.5) and
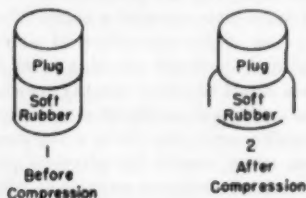
Fig. 1.—Uniaxial compression of a cylinder consisting of a plug (upper portion) and rubber (lower portion).

consequently expanding sideways, will in the joint zone be in a different state of stress than away from this zone. The same state occurs under the same conditions of deformation for any pair of materials having different values of lateral expansion under compression.

Let us consider another example. Let us subject to compression a test piece consisting of two cylinders with common axis (the compression forces are acting on the ends). In this case both the inner and the outer cylinder must expand in all lateral directions. If we disregard the influence of friction on the ends, which is always permissible for sufficiently thin and long cylinders (not exceeding of course, the limit of stability) it becomes clear that the difference in the lateral expansion causes stresses in the specimen. These stresses will be compressive or expansive depending on whether the Poisson's coefficient of the inner cylinder is greater or less than the coefficient of the outside cylinder. Consequently a simple alteration in the construction of the specimen, consisting of an alteration in position of the two materials, leads in the case under consideration to an alteration in the sign of the stress, which must have a considerable effect upon the resistance to ply separation.

These examples in no wise exhaust the question of the influence of the structure of a pliedup article upon its resistance to ply separation. Nevertheless one important conclusion arises from them. Any isotropic material exhibits two elastic characteristics. One of these—Young's modulus—is widely employed as a characteristic of vulcanized rubbers or cord. The second one,

for which we may select the modulus of shear, Poisson's coefficient or the modulus of volumetric compression, is not usually taken into consideration, since there is a widely held opinion that Poisson's coefficient is practically equal to 0.5 for all vulcanized rubbers, and in consequence of this only one independent elastic characteristic remains.

This assumption, arising probably on the basis of the kinetic theory of elasticity, which adopts as a basic function the maintenance of volume under deformation, is not accurate for actual vulcanized rubbers. The use of high-rigidity vulcanized rubbers obliges us particularly to stress this fact, since it is well known that Poisson's coefficient for hard polymers is considerably less than 0.5 (of the order of 0.3 to 0.4). In particular the polymers which go into the manufacture of cord have a value of Poisson's coefficient definitely lower than vulcanized rubber (we are not here considering the part played by the fiber as a structural element).

It must also be observed, that the difference in the values of Poisson's coefficient is not as small as is usually considered, since the whole range of alterations is 0.5, while the majority of solid materials differs by values of Poisson's coefficient within a limit of 0.2. In addition, as may be seen from the examples already given, in some cases only the Poisson's coefficient is of importance. With nonequivalence there is a qualitative change in the character of the distribution of the deformations and stresses. These alterations, even if of insignificant magnitude, lead in the process of repeated deformation to a considerable alteration in properties, as is generally characteristic of fatigue.

Thus it is necessary to turn our attention to the second elastic characteristic of vulcanized rubber, for instance, Poisson's coefficient and to consider the question of the conformity in the article not only of Young's modulus, but also of the Poisson's coefficients or, to put it more accurately, the combinations of these elastic characteristics corresponding to the structure of the article. It is possible that in individual cases (depending upon the pattern of service) it is necessary to adjust according only to one characteristic. Unfortunately this important question has so far not been worked out, and the values of Poisson's coefficient for vulcanized rubbers are in point of fact known only approximately.

In conclusion we must deal with one more question. It is known that there are different methods of determination of bond strength. The diversity of these methods has now brought about a need to analyze them in order to establish a connection between their results and service data. Since the fatigue of the boundary layer depends upon the pattern of deformation, it is natural that in many cases it is very difficult to find this correspondence, and sometimes impossible. It is clear nevertheless that the illustration of the mechanism of fatigue of the boundary layer makes it possible in turn to reveal an internal connection between the results of testing by various methods. At present the data for solving this very important problem are still inadequate.

Nevertheless it is necessary to begin such a series of investigations; it is necessary to use the already existing information about bond strength. First of all there arises the question of the relationship between static and dynamic methods of bond strength testing. There cannot be a simple relationship between these methods and this is confirmed by experience. In point of fact, in static testing the plied up specimen undergoes ply separation in the state in which it is made. At the same time in dynamic testing the specimen is subjected to repeated deformations, i.e., is fatigued, and its properties alter. This fatigue may become evident either in the development of a complete complex of processes which alter the structure of the material and lead to the growth of

micro defects, and in the growth of already existing micro defects. In either case the difference between static and dynamic tests of bond strength is that in the dynamic test there is a development of the fatigue process. Depending upon the strictness of the conditions of dynamic testing, the process of fatigue develops in one or other form or degree. The outcome is that on the one hand it is possible to approximate the several types of dynamic testing to the static, and on the other hand it is not possible to expect conformity of results from the different dynamic tests.

From all the above there emerges the necessity of a more profound study of the processes of fatigue of vulcanized rubber in general, and of the boundary layer in particular. We must more profoundly study the physical chemical processes which develop during fatigue, and investigate the conditions of formation and growth of micro defects. The analysis of the data on bond strength obtained by various methods must be carried out with due regard to the phenomena of fatigue and the conditions of deformation, determined by the construction of the specimen, the elastic characteristics of the pliedup materials and of the boundary layer, and also by the external conditions of influence.

CONCLUSIONS

1. Ply separation of multiply specimens and articles, operating under conditions of repeated deformation, is a result of fatigue of the boundary layer.

2. The development of the process of fatigue is determined by the structure and composition of the fatigued material, and also by the pattern of action.

3. The difference of fatigue of the boundary layer from the fatigue of uniform masses of material is governed by their difference in composition and structure, and also by the difference in the patterns of deformations of the boundary layer and of the uniform materials.

4. The formulation, technological and physical chemical factors, which influence each other mutually, determine the structure and compositions of the boundary layer which is eventually formed in the process of contacting the surfaces and vulcanization.

5. The pattern of action of the mechanical forces upon the boundary layer is determined by the applied external forces or deformations, by the construction of the multiply specimen or article and by the ratio of the elastic characteristics of the material (Young's modulus and Poisson's coefficient).

6. The formation of principles of a theory of bond strength between the elements of multiply articles is possible only by ascertaining the mechanism of fatigue of the boundary layer. For this we require the investigation of the viscoelastic properties of the raw stocks, of the phenomena which take place at surfaces of uniform raw stocks and of pliedup raw stocks, and of the process of vulcanization in the boundary layer. All these questions must be investigated as a complex, i.e., with consideration of the internal bonds existing between the formulation, technological and physical chemical factors. In addition it is necessary to analyze the influence of the construction and the elastic properties of the materials upon the character of the stresses, which arise in the joint zone.

7. A further major task in the theory of bond strength is the theoretical consideration of the nature of the tackiness of raw stocks and of the mechanism of the action of bonding agents.

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REINFORCEMENT OF RUBBER BY FILLERS
TEAR RESISTANCE*

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INTRODUCTION

Physical studies of the nature of reinforcement of rubber produced by the incorporation of fine particulate fillers fall naturally into two groups. The first is concerned with stiffness and the second with strength. The stress-strain behavior of filler reinforced vulcanizates has been extensively examined and, although certain anomalies still remain, the source of the increase in stiffness produced by fillers is fairly well understood. The position with regard to strength properties is far less satisfactory. Large increases in strength and abrasion resistance may be obtained by the addition of reinforcing fillers to rubbers which do not crystallize on stretching. With crystallizing rubbers the increases in strength qualities produced by fillers are not so pronounced and crystallization is itself regarded as providing some measure of reinforcement. Little advance has previously been made in determining the source of these increases in strength.

This importance of both the crystallization of rubber on stretching and the presence of fine particulate fillers on strength provides an interesting paradox. At first sight it is surprising that the introduction of rigid particles may result in greater strength. When rubber is strained these will produce either holes, if they are not wetted by the rubber, or alternatively, high stress concentrations, if they are wetted by the rubber. The obvious consequence of both of these possibilities is that the rubber should be weaker. Recent work at the B.R.P.R.A. has provided three clues which go some way towards unravelling this paradox.

EFFECT OF FILLERS ON ENERGY OF TEARING

The first is provided by Greensmith's work on the tearing of filler reinforced rubbers[1, 2, 3]. It was found that the tearing energy varied greatly with the type of rubber, nature of filler, and rate and temperature of tearing. Figures 1 and 2 show typical data on the effect of change in the rate of tearing on values of the tearing energy of both gum and HAF black reinforced vulcanizates of natural rubber and SBR respectively (Mixes A, B, C and D). Measurements were made using a 'trousers' shaped test piece previously described.

With the SBR gum vulcanizate the value of the tearing energy increases steadily with increased rate of tearing, but with the black vulcanizate the large increase in strength resulting from the black, which is shown at lower rates of tearing, is substantially reduced at higher rates. With the natural rubber vulcanizates the reinforcing action of both crystallization and fillers diminishes rapidly at higher rates of tearing. A pronounced difference in the tear be-
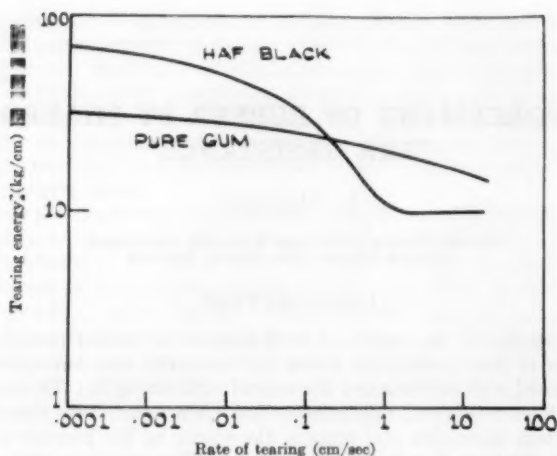
FIG. 1.—Effect of rate of tearing on the strength of natural rubber vulcanisates (25° C).

havior of the black rubbers is also apparent as the rate is increased from low to high values. At low rates of tearing, where the black is strongly reinforcing, the tear proceeds in a stick slip fashion and in some cases is knotty, whereas at high rates the tear proceeds steadily and the torn surfaces are much smoother.

Recently Greensmith[4] has shown that the increase in the roughness of the torn surfaces reflects a broadening of the tip of the growing tears. The tearing energy was shown to be simply related to the strength of rubber as measured in tensile rupture tests, and was the work required to stretch a small zone of rubber at the tip of the tear to rupture. The size of the zone depended on the effective diameter of the tip of the tear. Comparisons of tear and tensile
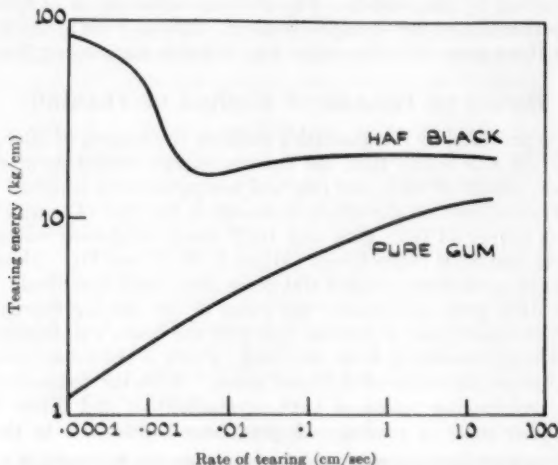
FIG. 2.—Effect of rate of tearing on the strength of SBR vulcanisates (25° C).

rupture data over a wide range of conditions of rate and temperature gave for the SBR gum vulcanizate an effective diameter of the tip of the tears of a few tenths of a millimeter. With the HAF black vulcanizate similar values of the effective diameter were required to fit tear and tensile rupture measurements in the absence of knotty tearing. At low rates of tearing, where knotty tearing developed, much larger values of the effective diameter of several millimeters were required and these were confirmed by direct measurement of the tip diameter. The changes in the effective diameter were also paralleled by observed changes in the roughness of the torn surface.
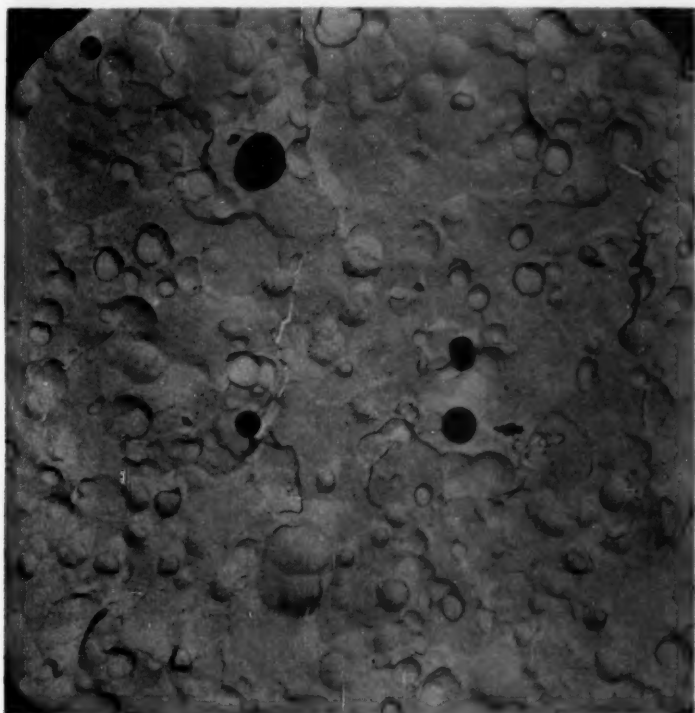
Fig. 3.—Rupture surface in brittle fracture of MT black vulcanizate.

It appears that when fillers result in a roughening of the torn surface and broadening of the tip of the growing tear they produce large increases in the tearing energy. Further, the maximum reinforcing effect of fillers is only exhibited during tearing if sufficient time is allowed for them to develop this strengthening charactersitic.

ELECTRON MICROSCOPY OF RUPTURE SURFACES

Although measurements of the macroscopic tear behavior described above show the effect of fillers on the strength of rubbers they do not reveal the mechanism which results in the enhanced strength. In an attempt to provide

information of this type Andrews and Walsh[5, 6] have recently studied the
rupture surfaces of carbon black loaded rubbers using replica electron micro-
scopy. Rupture surfaces were produced under a variety of conditions in a
range of black reinforced rubbers. These were replicated using a two stage
procedure in which gelatin was employed as a first stage and evaporated carbon
as a second stage. The latter was then examined in an electron microscope.

Figures 3 and 4 show rupture surfaces obtained in the brittle fracture and
slow tearing respectively of a rubber containing MT black, and Figure 5 shows
the surface obtained in slow tearing on rubber containing HAF black (mixes
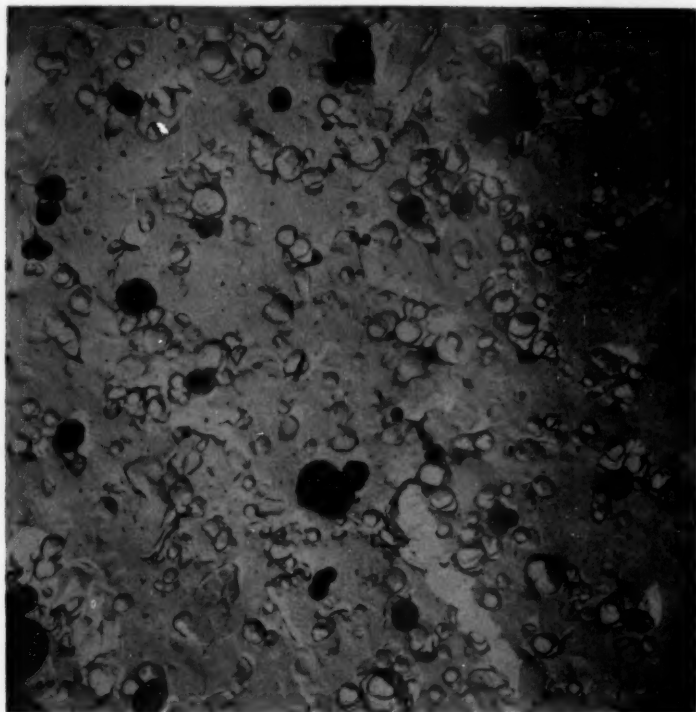
Fig. 4.—Rupture surface in slow tearing of MT black vulcanizate.

E and B). From these and other micrographs estimates were obtained of 1)
the proportion of the area of the replica occupied by particles of extracted black,
and 2) the total proportion of black, both extracted and replicated, in the
rupture surface.

The results showed a marked dependence of both of these quantities on the
mode of rupture and the type of carbon black. The amount of black extracted
during replication was greatest in slow tearing and least in brittle fracture and
was less the more reinforcing the black. This provided a relative measure of
the adhesion between rubber and carbon black and showed that adhesion is
greatest with more reinforcing blacks. Values of the total black were always

found to be higher than the actual loading of filler.   This difference was greatest in slow tearing and least in brittle fracture and indicated that the rupture surface was not a simple plane through the rubber but that the rupture path tended to travel from filler particle to filler particle.   This wandering of the rupture path was also clearly confirmed by stereoscopic examination and it appears that it preferentially seeks out the interface between rubber and black particles.
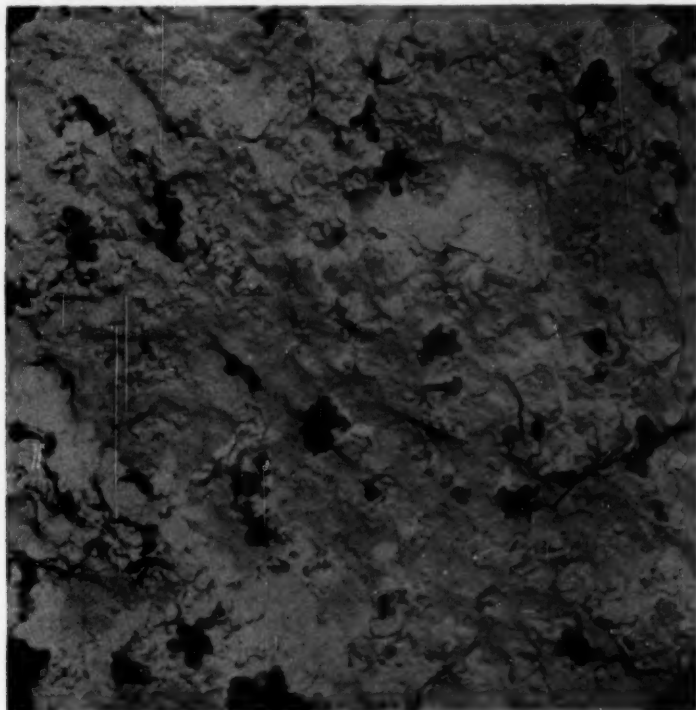
Fig. 5.—Rupture surface in slow tearing of HAF black vulcanizate.

These observations confirm that, as anticipated, the surface or immediate environment of filler particles is a zone of relative weakness.   Classical theory gives a maximum stress at a spherical boundary of three times the nominal stress.   It appears that failure takes place at these sites of relative weakness ahead of the advancing tip of the rupture and that its path wanders from one resulting internal flaw to another.   This produces the surface roughness and the high value for total filler observed in the electron microscope examination of ruptured surfaces.

These observations direct attention to one possible source of the strengthening action of fillers.   Multiple internal failure of the type described above gives rise to extra interfacial surfaces and a consequent increased dissipation of

energy. The results also draw attention to the importance of rubber to filler adhesion as the amount of elastic strain energy released by internal failure will depend upon how well the filler adheres to the rubber. The net result of fillers which adhere strongly is an enlarging of the volume of rubber which must be highly strained during the process of rupture.

EFFECT OF HYSTERESIS ON ENERGY OF TEARING

In the absence of reinforcement due to fillers or crystallization, the tear quality of rubbers is dominated by their hysteresial properties[7]. Under these circumstances the dependence of the tearing energy on rate and temperature
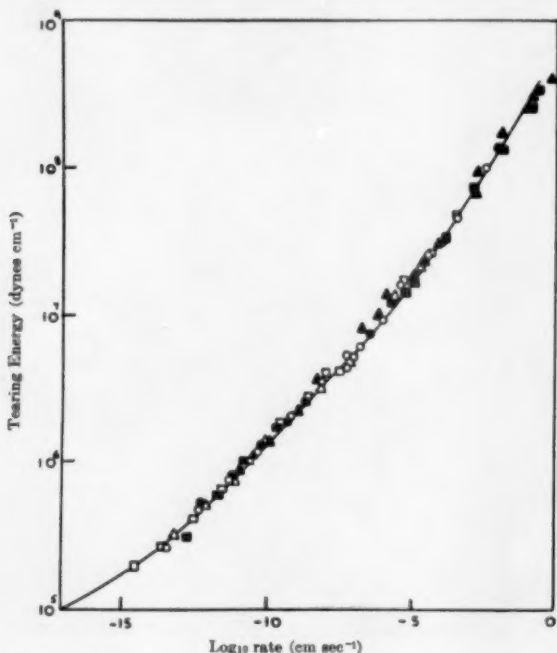
FIG. 6.—Transformed tearing energy data for butadiene-styrene and butadiene, acrylonitrile copolymers. Butadiene/styrene: △ 96/4; □ 87.5/12.5; ○ 71.5/12.5; Butadiene/Acrylonitrile: ● 82/18; ■ 70/30; ▲ 61/39.

followed the general pattern expected for a viscous type process. Using a rate-temperature transform of a type similar to that employed by Ferry to describe the interdependence of rate and temperatue for viscous and viscoelastic properties it is possible to describe the tearing energy of a wide range of gum vulcanizates of noncrystallizing butadiene-styrene and butadiene-acrylonitrile rubbers by a single curve. The results are shown in Figures 6 and 7 and indicate that the tearing energy of these rubbers is controlled by their chemical composition only insofar as the latter affects their second-order transition temperatures.

The success of this rate-temperature transform shows the important role of relaxation processes in determining the value of the tearing energy during the
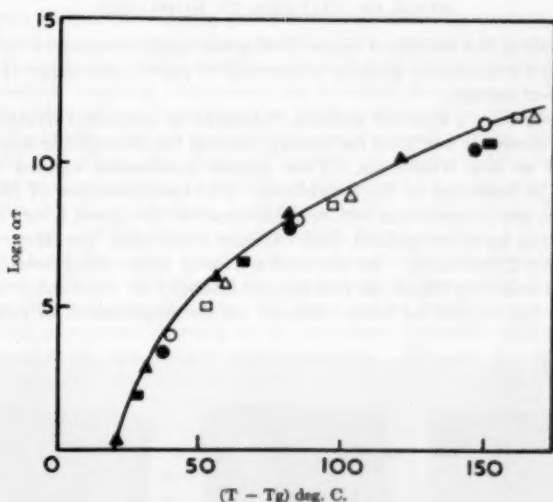
FIG. 7.—Rate—temperature transform.

steady tearing of rubber.   This feature is also demonstrated in Figure 8 which shows values of the tearing energy determined at 25° C at low 0.0025 cm/sec and high 25 cm/sec rates of tearing.   These are plotted as a function of the imaginary part of the complex shear modulus, which was also determined at 25° C and was derived from the damping of oscillations of a torsion pendulum with a period of approximately 2 seconds.   The figure shows a simple direct proportionality between the value of the tearing energy and the damping. Rubbers with higher hysteresis possess higher tear strength.
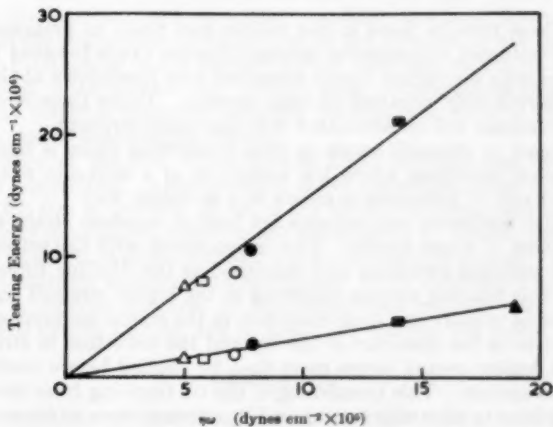
FIG. 8.—Dependence of tearing energy on damping.

ROLE OF FILLERS IN RUPTURE

A synthesis of the results of these three investigations can now be attempted and provides a qualitative picture of the role of particulate fillers in increasing the strength of rubber.

It has been shown that for unfilled vulcanizates increased hysteresis results in increased strength and that for steady tearing the strength is approximately proportional to the hysteresis. This simple conclusion cannot be applied directly to the behavior of filled rubbers. The incorporation of fillers always results in increased hysteresis but in many cases it also gives a loss in strength, but it has long been recognized that rubbers containing the more reinforcing fillers are more hysteresial. An obvious source of these differences in behavior is that nonreinforcing fillers do not adhere strongly to the rubber and are detached from the rubber to form vacuoles on the application of relatively low
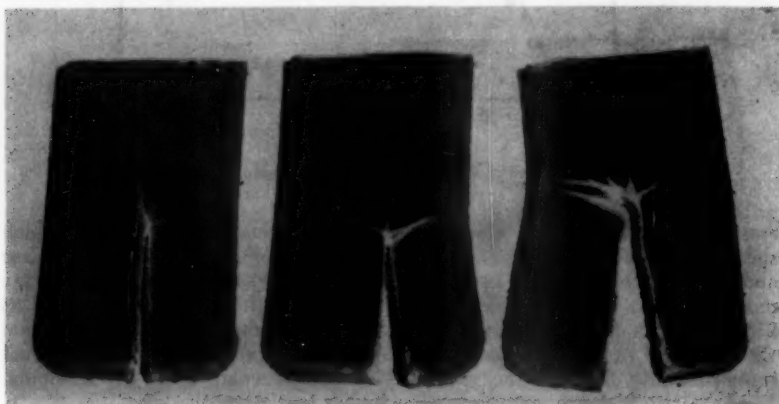
FIG. 9.—Tearing of rubber which softens on extension.

stresses. These provide flaws in the rubber and result in premature failure. With filler reinforced vulcanizates strong adhesion exists between the rubber and filler and with the carbon blacks examined here breakdown at the interface leading to flaws is only apparent at large stresses. Under these circumstances increased hysteresis will be associated with increased strength.

The increase in strength resulting from reinforcing fillers is much more in evidence under conditions where the rupture is of a stick-slip nature. Here an important role of hysteresis is shown in a revealing way.

When filler reinforced vulcanizates are held at constant strain a large and rapid relaxation of stress occurs. This is associated with the softening which results from previous extension and described as the Mullins Effect. A consequence of this relaxing process occurring in the highly strained region at the tip of a growing rupture is a local reduction in the elastic modulus and as a result an increase in the diameter of the tip and the reduction in stress concentrations. A higher overall stress must then be applied before further growth of the rupture occurs. This broadening of the tip resulting from the relaxation of stress will lead to stick-slip tearing and in extreme cases to branching of the rupture path.

The course of such a relaxing process during stick-slip tearing can be followed by direct examination of the growth of the tear and is demonstrated in Figure 8.   For purpose of demonstration a rubber showing pronounced softening over a narrow range of extensions was selected, and to assist in its visual representation the rubber was chosen to show a distinctive change in color on softening.   Figure 9(a) shows the early stages in growth of a tear from a sharp razor cut, the fine white line ahead of the tip shows the region of maximum stress and the commencement of change in color due to softening in this region. Figure 9(b) shows the next stage, further softening of the rubber has occurred and extended over a much wider region near the tip of the tear.   This reduction of modulus of the rubber has resulted in a large and obvious broadening of the tip of the tear.   Figure 9(c) shows the final stage of branching of the tear resulting from this relaxing process.   Its direction of travel has now changed from the initial one to one starting at the boundary between rubber which had softened considerably and rubber which had not.   The new tip of the tear is sharp once again and the process repeats.   At high rates of tearing little opportunity is given for this relaxing process to occur and the tear does not deviate from its original path.   Under these conditions broadening of the tip of the tear does not occur and the reinforcing role of relaxation of stress ahead of the tear has no opportunity to develop.

It appears that any hysteresial processes giving rise to sufficiently rapid stress relaxation ahead of the tip of a growing tear can in principle result in broadening of the tip of the tear and other things being equal lead to increased strength.   It is considered that this type of process plays an important and sometimes dominant role in the reinforcement of rubbers by fillers or by crystallization.   With filler reinforced rubbers softening due to extension occurs at low and moderate stresses and present evidence indicates that in these circumstances no actual detachment of filler and rubber occurs.   This system permits relaxation of stress at the tip of a tear, and its associated broadening, without the development of flaws at the rubber filler interface. Similarly with rubbers which crystallize on extension relaxation of stress occurs without the development of flaws.

The electron microscope study showed that at very high stresses breakdown occurred at the interface between rubber and filler, this breakdown in addition to leading to the dissipation of energy due to the creation of new surfaces and the possible lengthening of the overall rupture path also results in a relaxation of stress ahead of the rupture tip.   Under these circumstances this relaxation of stress may result in enhanced strength provided the flaws at the interface do not give rise to catastrophic failure.

This picture of the role of reinforcing fillers in increasing the following interrelated phenomena: 1) hysteresis, 2) stress relaxation ahead of the rupture tip, and 3) the size of the zone ahead of the tip which is involved in rupture is still necessarily qualitative, and it is not yet possible to discuss quantitatively the relative importance of the different complementary processes.   However, it provides a consistent and coherent mechanism which indicates a source of the roughening of rupture surfaces of filler reinforced rubbers and of possible branching and knotty tearing, and in good part resolves the initial paradox.

DISCUSSION

The incorporation of reinforcing fillers into rubber results in large increases in stiffness.   The mechanism, proposed here, which leads to an associated in-

crease in strength requires that much of this increase in stiffness should be capable of being destroyed during simple extension. It is considered that this mechanism, which involves stress relaxation ahead of the rupture tip, is important under conditions in which there is a large degree of reinforcement in strength and in which knotty or stick-slip tearing is shown. Apart from the physical disruption of rubber from filler particles no evidence has been put forward as to the exact nature of other hysteresial processes which result in this type of behavior. But to obtain the required degree of relaxation of stress it is necessary that large differences should exist between stress strain curves obtained during initial extension and during subsequent retraction.

It has been shown that good adhesion between rubber and filler is associated with high strength and most previous work has been concentrated on the nature of the interaction between rubber and fillers. It is now generally agreed that chemical interaction between rubber and carbon black occurs during mixing procedures[8, 9, 10, 11, 12]. The main evidence for this interaction is the formation of a gel in unvulcanized black rubber mixtures, and it has been claimed that the superior reinforcing ability of carbon blacks over other fillers is due to the presence of groups capable of accepting free radicals on their surfaces during mixing. The validity of this claim has yet to be established, and it has been shown that considerable reinforcement due to carbon black remains after chemical modifications of the filler particle surfaces designed to suppress free radical attachment[13].

In addition the possibility of vulcanization effecting rubber to carbon black combination has been suggested; such a process would not necessarily involve free radicals[8, 13].

It is considered that although strong bonding between rubber and filler is essential for high strength, the strength of the bonds will be unimportant in determining hysteresial processes which occur at stresses insufficient to break them. It is also considered that under certain conditions these hysteresial processes may dominate rupture behavior.

ACKNOWLEDGMENT

SUMMARY

The results of experimental studies on 1) the effect of reinforcing fillers on tear strength and on the roughness of the resultant torn surfaces, 2) the relative adhesion of rubber to fillers and 3) the effect of hysteresis on tear strength are critically examined. They show that the maximum reinforcing effect of fillers is only exhibited if sufficient time is allowed for their strengthening role to develop during tearing, and that under these conditions the tip of the growing tear is broader and the torn surface rougher. They also confirm that the surface or immediate environment of filler particles provide a region of relative weakness, and that failure takes place at the interfaces ahead of the advancing tear, the rupture path wandering from one internal flaw to another. In addition they show that the more reinforcing fillers adhere more strongly to the rubber. Further, for gum vulcanizates, it appears that there is a simple relationship between tearing energy and hysteresis and that rubbers with higher hysteresis possess higher tear strength.

A synthesis of the results of these three investigations provides a qualitative picture of the role of reinforcing fillers in increasing the strength of rubbers. It appears that a process giving rise to sufficiently rapid relaxation of stress ahead of the tip of a growing tear can in principle result in broadening of the tip of the tear and lead to increased strength. It is considered that this type of process plays an important and sometimes dominant role in the reinforcement of rubbers by fillers or by crystallization, and provides a consistent and coherent mechanism which indicates a source of the roughening of rupture surfaces of filler reinforced rubbers and of their possible branching and knotty tearing.

APPENDIX

COMPOUNDING DETAILS AND VULCANIZING PROCEDURES

Mix	A	B	C	D	E
			Parts by weight		
Smoked sheet	100	100	—	—	100
SBR	—	—	100	100	—
Zinc oxide	5	5	5	5	5
Sulfur	2	3	1.75	1.75	3
Stearic acid	1	3	2	2	3
MBT	1	1	—	—	1
CBS	—	—	1	1	—
Antioxidant	1	1	1	1	1
MT black	—	—	—	—	50
HAF black	—	50	—	50	—
Period and temperature of vulcanization	45 mins at 140° C	45 mins at 140° C	50 mins at 145° C	50 mins at 145° C	45 mins at 140° C

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VULCANIZATION OF ELASTOMERS. 24. THE EFFECT OF FILLERS ON THE COURSE OF VULCANIZATION REACTIONS. I *

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INTRODUCTION

All the investigations[1] we have made up to now relating to the kinetics of vulcanization reactions have been aimed, on the one hand, at explaining the mechanism and providing quantitative information for practical considerations, so as to make possible an evaluation of the chemical processes involved in vulcanization. On the other hand, our research had as its object the accumulation of test data based on quantitative determinations which might serve as a starting point for a systematic compounding program. Such being the goals, it was only natural that we study first of all the kinetics of vulcanization reactions occurring in the absence of all additives which are not absolutely necessary.

In the meantime our work had progressed to the point where we could also begin to consider vulcanizations in the presence of fillers important for practical vulcanizates. The present work is the first contribution in this field; and since thiuram vulcanization has been heretofore the most thoroughly studied[2] we began this series with an investigation of the kinetics of such vulcanizations in the presence of a highly-dispersed silica gel, Aerosil.

The experiments, begun with natural rubber, have by no means been completed, but we do feel a preliminary report is in order because of the noteworthy results already obtained[3].

The answer to the question as to the origin of the activity displayed by so-called "active" fillers, capable of enhancing the physical properties of vulcanizates, has of late aroused lively interest and activity in our field. Numerous publications have appeared, concerned both with the experimental and theoretical aspects of the interaction between filler surface and polymer, and it would be impossible to comment here on even the better contributions. Besides, it is not imperative that they be discussed at this point, since the present work is concerned with what we consider to be the more neglected feature, namely, the influence of fillers on the course of the vulcanization.

EXPERIMENTAL AND RESULTS

In order to preserve the continuity of our quantitative studies of thiuram vulcanization, we continued to use pale crepe extracted exhaustively with acetone in a Soxhlet apparatus. Each 100 g of mixture contained 2.96 g of tetraethylthiuram disulfide (TETD) and 5 g ZnO (active); in addition, either a 5 g or 10 g quantity of Aerosil was added. When the rubber compounds were

mixed, Degussa Aerosil (silica gel) and zinc oxide were first added, the mill roll temperature being 50° C.   TETD was then blended in with cooling of the rolls. Care was taken to keep experimental conditions as constant as possible when the mixes were prepared because preliminary experiments had shown that especially the values for reciprocal equilibrium swelling were subject to considerable fluctuation unless such precautions were taken.   These previously unnoticed complications are presumably due to the interaction between Aerosil and rubber (sorption, formation of bound rubber) accompanied, when uncontrolled, by scattering and poor reproducibility of the test results in general, especially of the swelling, which is sensitive under any circumstances.
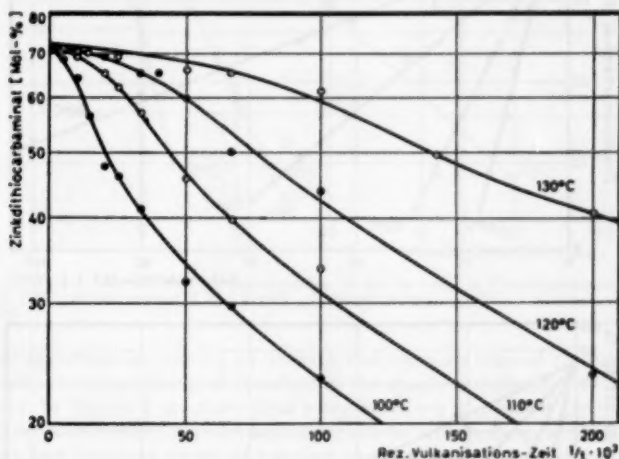
Fig. 1.—Demonstration of the limiting value of dithiocarbamate formation in the vulcanization of natural rubber with TETD (tetraethylthiuram disulfide) in the presence of Aerosil.   Ordinate: zinc dithiocarbamate (mole %).   Abscissa: reciprocal of vulcanization time $1/t \cdot 10^3$.

We became convinced that a rubber mixture containing only a certain amount of Aerosil and zinc oxide will not dissolve in benzene anymore if subjected to prolonged heating at 140° C, from which it follows that the two oxides alone are responsible for a certain modification of the molecular network; yet this modification cannot be extensive, since an extraordinary degree of swelling in benzene takes place as compared to that of unfilled vulcanizates.

We now became interested in whether Aerosil had any effect on the reactions observed in thiuram vulcanizations.   Figure 1, in which the formation of zinc dithiocarbamate (ZnDC) is plotted against the reciprocal vulcanization time, shows that the limiting value of dithiocarbamate formation is rather high and amounts to about 72 mole % (with respect to the initial amount of thiuram disulfide), whereas, in the absence of silica gel, this value has always been around 66 mole %.   This is surely not the result of faulty analysis, especially since the quantitative determination of the ZnDC was made by means of both conductometric titration and spectrophotometry, with excellent agreement of the results.   However, we are not yet ready, in this connection, to offer a possible explanation for the higher limiting value.

Figures 2a and 2b show the formation of dithiocarbamate, the test results

being plotted according to a first order law. In both instances the com-
pounds had the same composition and contained 10 g Aerosil apiece. The
results portrayed in Figure 2a came from a single batch, while the four curves
in Figure 2b correspond to four different batches. Without a doubt, even
in the presence of Aerosil, the dithiocarbamate formation will follow a law
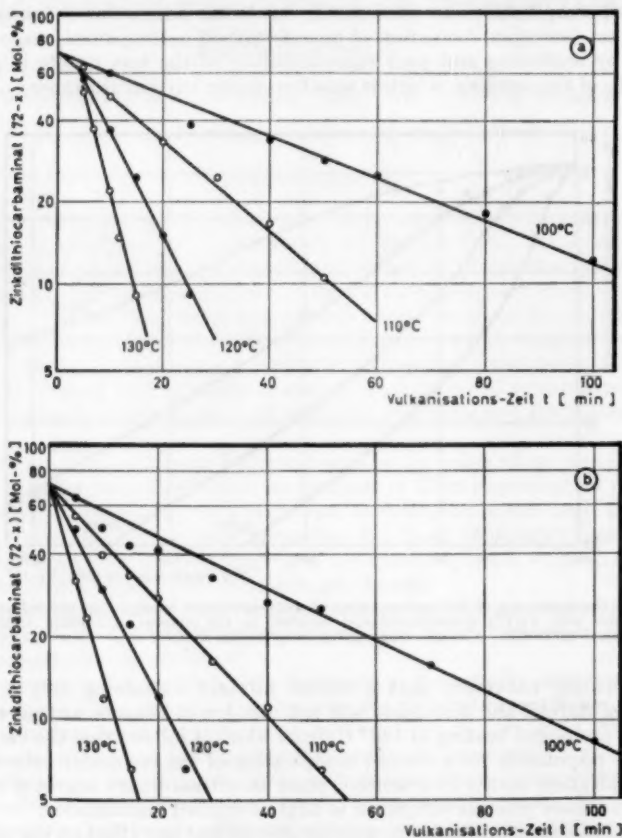
Figs. 2a and 2b.—Dithiocarbamate formation plotted according to the 1st order in the vulcanization
of natural rubber with TETD in the presence of 10 g Aerosil. (2a: results obtained with only one initial
batch; 2b: four separately compounded batches.) Ordinate: zinc dithiocarbamate (72-z) (mole %);
Abscissa: Vulcanization time t (min).

of the first order in by far the greatest range of conversions, but the scat-
tering of the points from the straight lines is greater, for the reasons mentioned,
than in tests where no silica gel is used, and is particularly noticeable at lower
temperatures (cf. the curve for 100° C in Figure 2b). The measurements repre-
sented by Figure 2a, for vulcanizates derived from a single batch, should be
more precise, even though the curves for 120° C and 130° C do not intersect
the ordinate for t = 0 at 72 mole %, this being no doubt attributable to un-
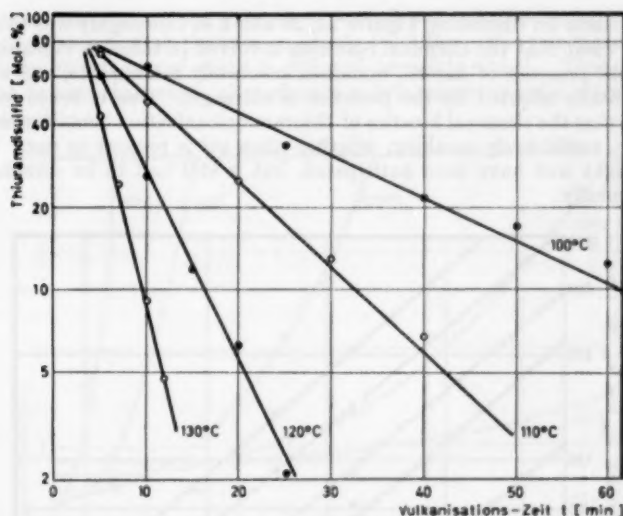
FIG. 3.—Thiuram disappearance plotted according to the 1st order in the vulcanization of natural rubber with TETD in the presence of 10 g Aerosil. Ordinate: thiuram disulfide. Abscissa: vulcanization time t (min).

avoidable uncertainties having to do with the warmup time of the steel molds which make the pinpointing of the start of the reaction difficult.

Finally, in Figure 3, we show that when silica gel is present, the disappearance of the thiuram also follows a first order law for a large range of the reactions. Here, too, one becomes aware of the fact that at lower temperatures the test results show scattering. Nevertheless, the linear dependence on the vulcanization time, of the log of the TETD still present, is unmistakeable.

TABLE I

FIRST ORDER RATE CONSTANTS FOR THIURAM DISAPPEARANCE k_{TD}^1 AND DITHIO-CARBAMATE FORMATION k_{DC}^1, AS WELL AS THE ACTIVATION ENERGIES Q_{DC} AND Q_{TD} RESPECTIVELY IN THE VULCANIZATION OF 92.04 G OF NATURAL RUBBER WITH 2.06 G OF TETRAETHYL THIURAM DISULFIDE IN THE PRESENCE OF 5 G ZnO AND x G AEROSIL ($x = 0; 5; 10$)

Vulcanization temp. °C	I $x = 0$ g Measurements of W. Scheele and G. Mau[7]	II $x = 5$ g	III $x = 10$ g cf. Figure 2a	IV $x = 10$ g cf. Figure 2b	V $x = 0$ g Measurements by O. Lorenz, W. Scheele and W. Redetzky[4]	VI $x = 10$ g Measurements from present work cf. Figure 3
	$k_{DC}^1 \cdot 10^3$ (min⁻¹)		Measurements from present work		$k_{TD}^1 \cdot 10^3$ (min⁻¹)	
100	2.2	12.1	18.0	21.8	6.3	35.6
110	4.0	23.2	39.0	49.0	10.9	70.9
120	10.6	50.3	89.3	89.6	26.8	161.0
130	16.0	85.3	174.5	162.1	61.4	311.0
140	34.6	131.5	—	—	—	—
150	61.9	—	—	—	—	—
	Q_{DC} (kcal/mole)				Q_{TD} (kcal/mole)	
	21.0	21.2	21.0	31.0	21.	21.4

Our reason for discussing Figures 2a, 2b and 3 so thoroughly was to make it perfectly clear that the chemical reactions involved in thiuram vulcanizations, even in the presence of Aerosil, remained accurately mensurable, and were not fundamentally affected by the presence of silica gel.   One is hence forced to conclude that the chemical kinetics of thiuram vulcanization remain practically the same, *qualitatively* speaking, whether silica gel is present or not.   Such a result might well have been anticipated, but it still had to be demonstrated experimentally.
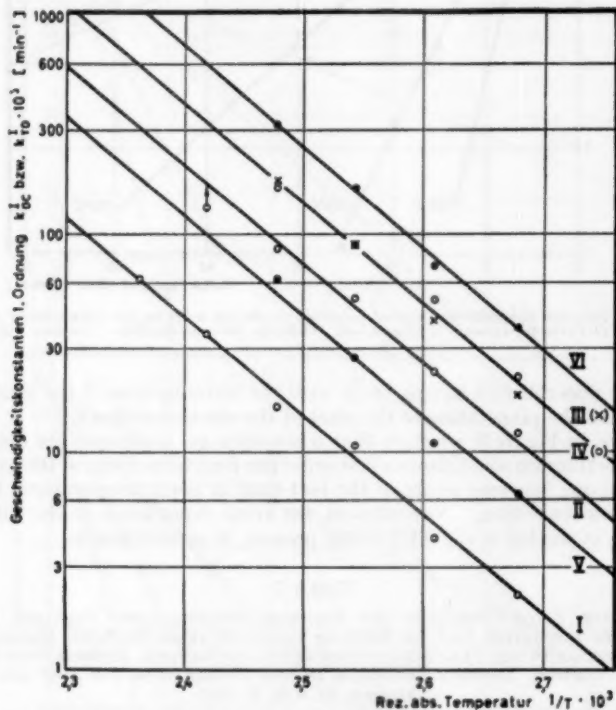
Fig. 4.—Rate constants for thiuram loss k_{TD} and dithiocarbamate formation k_{DC} in the vulcanization of natural rubber with TETD in the absence or presence of Aerosil.   I: k_{DC} (no Aerosil); II: k_{DC} (5 g Aerosil); III and IV: k_{DC} (10 g Aerosil, two test series); V: k_{TD} (without Aerosil); VI: k_{TD} (10 g Aerosil). Ordinate: 1st order rate constants k_{DC} or $k_{TD} \cdot 10^3$ (min^{-1}).   Abscissa: reciprocal of absolute temperature $1/T \cdot 10^3$.

Essential changes appear, however, from a quantitative standpoint.   In Table I are assembled the rate constants for dithiocarbamate formation and thiuram loss when vulcanization takes place in the presence or absence of Aerosil.   In our opinion the figures in the table disclose an important fact: the presence of silica gel induces an extraordinary rise in the rate constants for dithiocarbamate formation and thiuram disappearance.   When 10 g of Aerosil has been introduced, the rate constants for thiuram disappearance and di- thiocarbamate formation are greater by factors of 5 . . . 6 and 9 . . . 10 respectively, than in the absence of Aerosil.   There is, besides, a dependence

of the rate constants on the amount of Aerosil put into the mixture; for it is clear from Table I, that the rate constants for dithiocarbamate formation increase only by a factor of about 5, if 5 g of Aerosil is added. Thus one is inclined to believe that what takes place is a heterogeneous catalysis *via* highly dispersed silica gel.
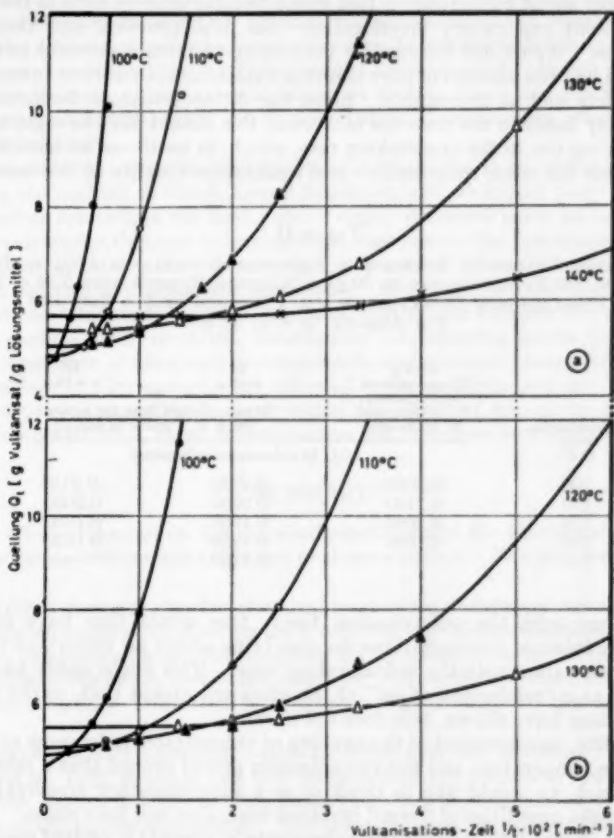
Figs. 5a and 5b.—Demonstration of limiting equilibrium swelling in the vulcanization of natural rubber with TETD in the presence of 5 g (5a) or 10 g (5b) of Aerosil. Ordinate swelling Q_t (g vulcanisate/g solvent). Abscissa: vulcanization time $1/t \cdot 10^2$ (min^{-1}).

But the catalysis of a chemical reaction is usually accompanied by a diminution in the energy of activation. A logarithmic plotting of the rate constants for thiuram disappearance and dithiocarbamate formation against the reciprocal absolute temperature gives, however, straight lines I to VI in Figure 4, bringing into evidence the phenomenal rise in rate constants, and allowing the calculation—from the slopes—of the activation energies, amounting to some 21 kcal/mole. Consequently there can be no mention of a lowering of the activation energy through the use of silica gel. Such a result is understandable, seeing

that even vulcanizations with thiuram alone represents a reaction activated by zinc oxide[4]. Scheele and Kemme[5], in fact, found that the speed at which thiuram disappears and dithiocarbamate is formed, when TETD reacts in solvents, is dependent on the degree of dispersion of the zinc oxide.

We feel that the unusually large increase in the speed of thiuram vulcanization brought about by Aerosil—a fact which became evident even in the course of the present exploratory investigation—has both practical and theoretical significance.   We do not believe this interesting phenomenon could have been discovered had the kinetics of pure thiuram vulcanization not been investigated so accurately and so thoroughly.   Since the dithiocarbamate formation goes considerably faster in the presence of Aerosil, this should have brought about a corresponding rise in the crosslinking rate, which, in itself—as we have recently shown[1]—has the same quantitative and qualitative kinetics as the increase in

TABLE II

The Limiting Values of Reciprocal Equilibrium Swelling $1/Q_\infty$ in Benzene (25° C) in the Vulcanization of 92.04 g Natural Rubber with 2.96 g Tetra-ethylthiuram Disulfide in the Presence of 5 g ZnO and x g Aerosil ($x = 0$; 5; 10)

	I $x = 0$ g Measurements by O. Lorenz, W. Scheele and W. Redetzky[4]	II $x = 5$ g	III $x = 10$ g
Vulcanization temp. (° C)		Measurements from the present work, cf. Figures 5a and 5b	
	$1/Q_\infty$ (g vulcanizate/g benzene)		
100	(0.2000)	0.2150	0.2150
110	0.2100	0.2050	0.2050
120	0.2000	0.1950	0.1950
130	0.1800	0.1850	0.1820
140	—	0.1750	—

stress values with the vulcanization time.   One would thus have expected Aerosil, in thiuram vulcanizations, to also bring about an important increase in the stress values with the vulcanization time.   This might easily have been explained as a "reinforcing effect" of the silica gel, except that, as the present investigations have shown, this does not occur.

In reality, measurement of the swelling of vulcanizates in benzene as a function of the temperature and the vulcanization period proved that a reinforcing effect (which we would like to think of as a supplementary crosslinking), at least with the quantities of Aerosil involved here, does not take place.   Figures 5a and 5b, in which the swelling (g vulcanizate/g solvent) is plotted against the reciprocal of the vulcanization time, show first of all that the limiting values for swelling (Q_∞) are practically the same, whether 5 g or 10 g of Aerosil is added.   They do show a slight dependence on temperature, but this has no significance for the present discussion.   Table II compares the reciprocal limiting equilibrium swellings $1/Q_\infty$ with those obtained with vulcanizations in the absence of silica gel.   It will be seen that the values are in good agreement and that the silica gel evidently does not affect the crosslink densities which are finally reached.   But because we have not, as yet, been able to obtain swelling data of sufficient accuracy to justify their evaluation for kinetic purposes, we are limiting ourselves for the present to the preliminary observation that, also in the case of thiuram vulcanizations with Aerosil, the changes in reciprocal

equilibrium swelling with the time can be depicted as first order processes, subsequent to an induction period.

Although the rate constants can only be estimated, nevertheless they should be derivable from the values which are determined for the dithiocarbamate formation.

In summation, then, one can say that the outstanding feature of the effect of highly dispersed silica gel on thiuram vulcanizations is the remarkable rise in the rate, a circumstance which can, of course, be substantiated only when the kinetics are known and the final conversions are compared.   Hence the stress values for thiuram vulcanizates obtained at similar times and temperatures, with or without Aerosil, ought not be looked upon as comparable, corresponding technological data.

We consider the experimental results presented here to be of some value in assessing the manner in which Aerosil functions, and we expect them to stimulate further research in the field.   Since highly dispersed silica gel has proved to be catalytic for thiuram vulcanizations, there exists the fundamental possibility of characterizing the different silica gels used as fillers, according to their catalytic activity in thiuram vulcanizations.   Above and beyond this, however, kinetic measurements of thiuram vulcanizations should also provide an insight into the part played by so-called "distributors" or dispersing agents (promoters) in the preparation of filled rubber compounds, and especially how modifications in the surface of filler particles are reflected in the catalytic activity.   Finally, it should prove interesting to know about the effect of Aerosil on other vulcanization reactions.   These investigations will therefore be continued.

SUMMARY

The effect of Aerosil on the chemical reactions and the kinetics observed in thiuram vulcanizations was subjected to closer scrutiny.   Results now available show:

1. Aerosil does not alter the chemical mechanism of thiuram vulcanizations. It also has no qualitative effect on the kinetics of the various reactions involved. Thiuram disappearance and dithiocarbamate formation over by far the greatest range of conversions are first order reactions.   Nevertheless, the limiting value of dithiocarbamate formation is somewhat higher than in the absence of Aerosil.

2. Quantitatively speaking, essential differences are involved.   The rate constants for both thiuram loss and dithiocarbamate formation rise considerably when Aerosil is used; in both cases there is a dependence on the Aerosil content of the rubber compound.   Yet the activation energies of thiuram disappearance and dithiocarbamate formation are practically the same as in Aerosil-free thiuram vulcanizations, amounting to about 21 kcal/mole.

3. Measurements of the limiting equilibrium swelling reveal that adding Aerosil does not result in additional crosslinking, so that in thiuram vulcanizations the catalytic action displayed by silica gel is the outstanding feature.

ACKNOWLEDGMENTS

number of fillers at out disposal.   To all who helped in this way we again wish
to express our sincere thanks.

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VULCANIZATION OF ELASTOMERS. 23. THE CHEMICAL KINETICS OF VULCANIZATION REACTIONS AND THE PHYSICAL PROPERTIES OF THE VULCANIZATES. I *

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INTRODUCTION

Previous publications in this series were concerned exclusively with the chemical kinetics of vulcanization reactions[1], but now and then the progress per unit vulcanization time of the reciprocal equilibrium swelling $1/Q_t$ (crosslinking) was brought into the picture, and each time an attempt was made to see if this process had any connection with the chemical reactions involved, and, if so, to determine with which of the chemical reactions its kinetics agreed, both qualitatively and quantitatively. For example we discovered that the change in the reciprocal equilibrium swelling in purely thiuram vulcanizations goes according to the first order, and that an equality in rate exists between this swelling and the formation of dithiocarbamate, which is also a first order process[2], i.e., crosslinking is dependent on the dithiocarbamate formation, but not on the increase in bound sulfur whose kinetics are of an entirely different sort[3].

Without question, reciprocal equilibrium swelling in the proper medium is a reliable criterion of the degree of crosslinking of a vulcanizate. For this reason the knowledge of its kinetics affords the possibility, in every case, of establishing a relationship between the course of the chemical reactions and the development of physical properties as vulcanization progresses. We investigated these relations, using as an example our heretofore most intensively studied vulcanization, that of natural rubber with tetraethylthiuram disulfide (TETD) in the presence of zinc oxide, at different temperatures. Our first concern was a more thorough study of the kinetics of stress values at various elongations.

EXPERIMENTAL AND DISCUSSION

Once again we used pale crepe, extracted exhaustively with acetone in a Soxhlet apparatus. During mastication and blending-in of zinc oxide and TETD we were most careful to see that both the breaking-down and the compounding times, as well as the temperature of the rolls, were kept as constant as possible, because any differences at all in the degree of breakdown of the rubber would show up later in the stress values of the vulcanizates. For this reason our general practice was to use a single batch for each test series conducted at a certain temperature. This provided a correspondence, at least within one particular series of experiments, between all of the stress values

measured. The mixes contained 5.92 g TETD, 10 g zinc oxide and 84.08 g natural rubber.

The vulcanized test pieces, died out from sheets some 0.85 mm thick, were strips, 3 mm wide and 120 mm long (gaged length: 100 mm). A specially designed apparatus measured the stress values at increasing degrees of extension and at constant deformation rates, or at a constant deformation period. It was assumed that it makes no great difference whether the measurements take place at the same deformation rate or the same deformation time, with higher degrees of vulcanization. But with vulcanizates which are only slightly crosslinked, deviations are observed, such as a drop in the stress values as the deformation time increases. The measurements were made at 110°, 120°, 130°, 135°, 140°, 145° and 150° C.
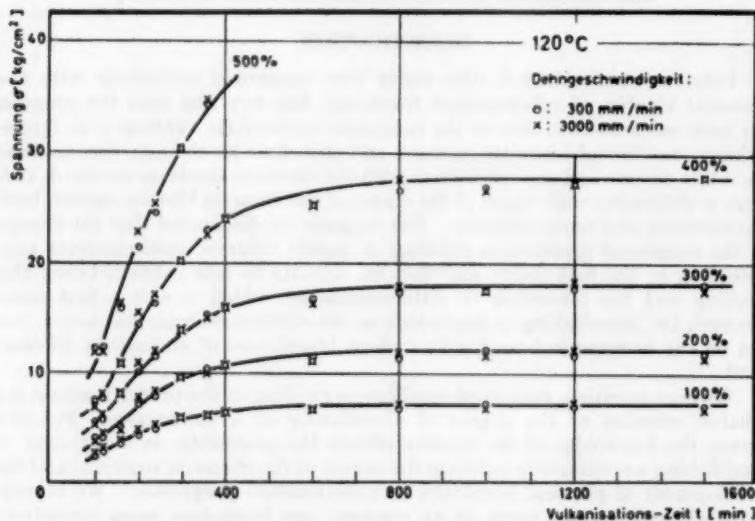
FIG. 1.—Rise in stress at different degrees of elongation in the vulcanization of natural rubber with tetraethylthiuram disulfide in the presence of ZnO at 120° C. Dehnungsgeschwindigkeit = rate of elongation. Ordinate: stress (kg/cm²); abscissa: vulcanization time t (min).

Figure 1 shows the variation in stress values at different elongations (100 to 150%) as a function of the vulcanization time at 120° C. For shorter reaction times a retardation or induction period in the start of crosslinking is noticed, followed by a rise in the stress values, along the arc of a continuous curve with an ultimate straightening out of the curve to practically constant end values. In any case, no vulcanization plateaus are formed such as are observed for many other vulcanization reactions.

The induction period for crosslinking agrees with the results of recent publications on the kinetics of the increase in bound sulfur in thiuram vulcanizations[3], namely, that up to the time the combined sulfur reaches a maximum, the vulcanizates display no technically useful physical properties, although the dithiocarbamate formation requires no noticeable incubation period and satisfies, at the beginning, the first order law. Since, however, the formation of dithiocarbamate seems to be connected with crosslinking, it is strongly suspected that the establishment of bridge bonds is widely inhibited at the beginning.

At higher temperatures the induction period of the rise in stress diminishes more and more, as can be seen from Figure 2, which presents corresponding measurements, at 150° C. This accords with the shifting of the maxima for the increase in bound sulfur into domains of shorter reaction periods at higher temperatures[3].

The stress values, increasing, of course, with increasing elongation, will, for a given extension, tend to reach a limiting value σ_∞ which is independent of the vulcanization temperature. This results from the two-thirds conversion of TETD to zinc dithiocarbamate. It is not dependent on the temperature but is connected with the crosslinking, giving rise, therefore, to a constant degree of
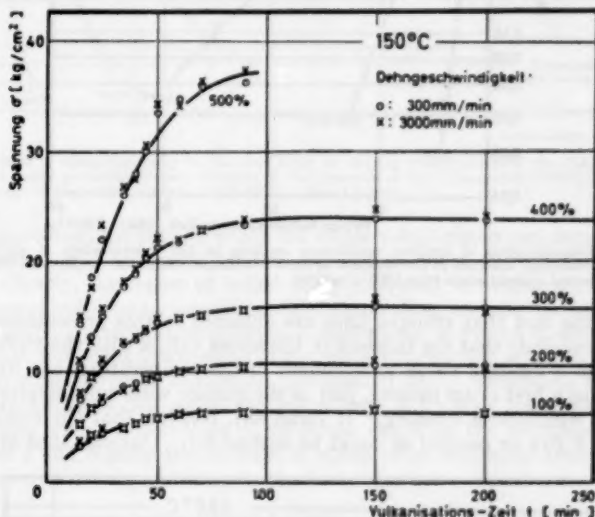
Fig. 2.—Rise in stress at different degrees of elongation in the vulcanization of natural rubber with tetraethylthiuram disulfide in the presence of ZnO at 150° C. Ordinate: stress (kg/cm²); abscissa: vulcanization time *t* (min).

crosslinking corresponding to the amount of TETD introduced. Evidently, however, this fact stands out only because the experimental conditions under which the vulcanizates were prepared were held so constant.

In Figure 3 we show that the crosslinking, too, approaches a limiting value that is practically independent of the temperature, the mean of this value, $1/Q_\infty$, being 0.273. With shorter vulcanization times, the reciprocal equilibrium swelling is also subject to retardation, but swelling is much too great and the crosslinking much too slight to be measured with any accuracy. We therefore relinquished any notion of plotting special curves for the time-dependent change in reciprocal equilibrium swelling, especially since such curves would correspond in every respect to those shown in Figures 1 and 2.

Figure 4 presents a logarithmic plot of the values of $(\sigma_\infty - \sigma_t)$ for elongations of 100, 200, 300, 400 and 500% (Curves I–V), in addition to the values for $(1/Q_\infty - 1/Q_t)$ (Curve VI), at 120° C, against the vulcanization time. It must be strongly emphasized here that what is presented in Figure 4 for the vulcanization temperature, 120° C, is also to be observed for all the other temperatures. The dashed line signifies the end of the crosslinking induction period.
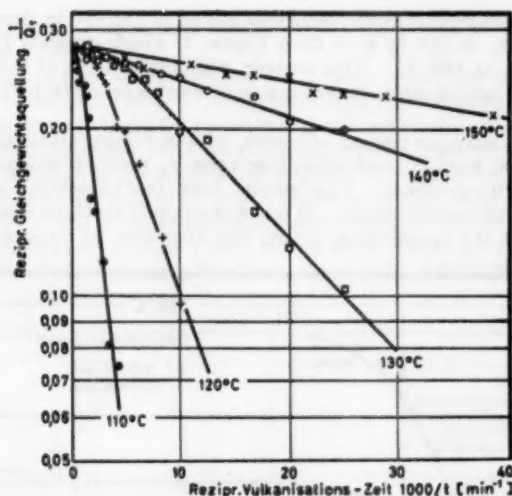
Fig. 3.—Demonstration of limiting equilibrium swelling in the vulcanization of natural rubber with tetraethylthiuram disulfide in the presence of ZnO. Ordinate: reciprocal equilibrium swelling $1/Q_t$; abscissa: reciprocal vulcanization time $1000/t$ (min^{-1}).

From the fact that straight lines are obtained in this presentation, one is forced to conclude that the increase in the stress values with the vulcanization time, up to a limiting value independent of the temperature, can likewise be described as a first order process, just as the change with vulcanization time in reciprocal equilibrium swelling. It turns out, besides, that the straight lines in Figure 4 run as parallel as could be wished for. One can thus arrive at a
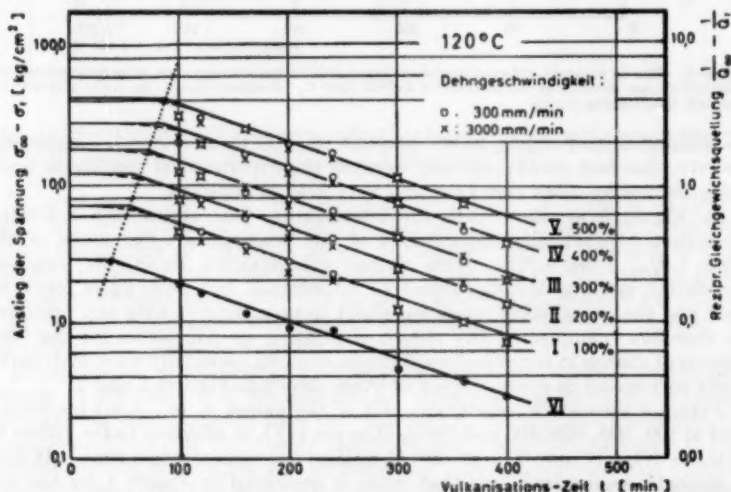
Fig. 4.—Rise in stress and reciprocal equilibrium swelling as a first order process in the vulcanization of natural rubber with tetraethylthiuram disulfide in the presence of ZnO ($T = 120°$ C). Ordinate: rise in stress $\sigma_\infty - \sigma_t$ (kg/cm^2); abscissa: vulcanization time t (min).
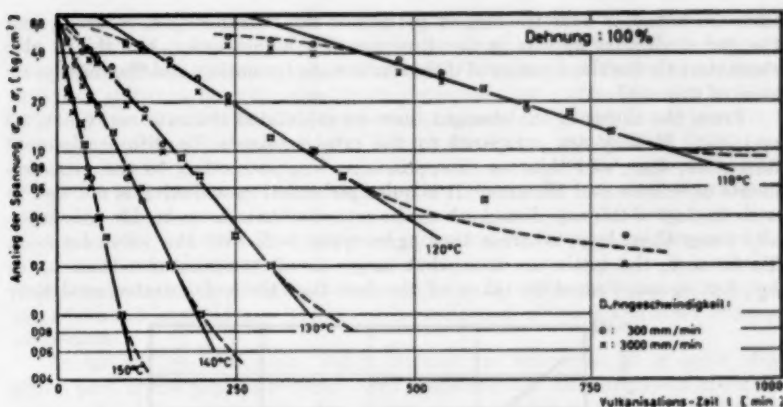
FIG. 5.—Rise in stress according to the first order at varying temperatures in the vulcanization of natural rubber with tetraethylthiuram disulfide in the presence of ZnO (elongation = 100%). Ordinate: rise in stress $\sigma_\infty - \sigma_t$ (kg/cm²); abscissa: vulcanization time t (min).

further conclusion: the rate at which the stress values rise is not dependent on the elongation, and the rates for the increase in stress and crosslinking are similar. Clearly, the region of initial delay is equally in evidence in the time dependence of both the reciprocal equilibrium swelling and the modulus values when the graphic presentation selected is that shown in Figure 4, accompanied by a distinct, but slight lengthening of the initial retardation period as the stress values rise with increased elongation (see dashed line). Doubtless this stems from the fact that in this region the vulcanizate still shows considerable flow; thus one also finds a dependence of the stress values on the deformation time.

Figures 5 and 6 show the increase in stress or in reciprocal swelling at all temperatures, plotted according to the first order law. In all cases, straight
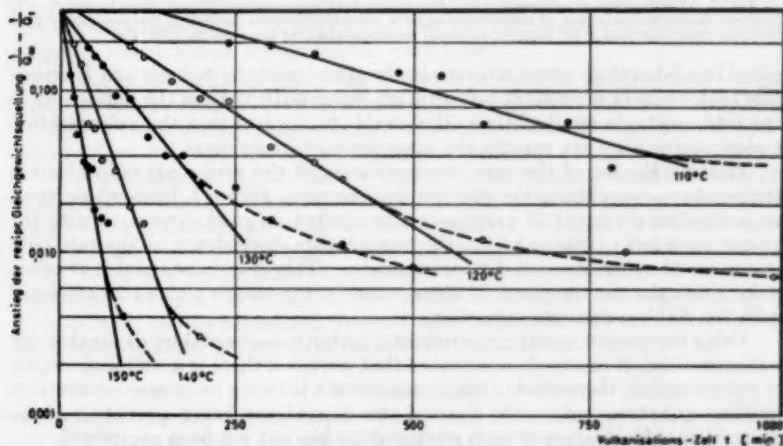
FIG. 6.—Time-dependent change in the reciprocal equilibrium swelling according to the first order at varying temperatures in the vulcanization of natural rubber with tetraethylthiuram disulfide. Ordinate: rise in reciprocal equilibrium swelling, $1/Q_\infty - 1/Q_t$; abscissa: vulcanization time t (min).

lines are obtained over the largest portion of the vulcanization, whereas near the end deviations appear in the direction of a higher order, but this is also characteristic for the kinetics of dithiocarbamate formation and the disappearance of thiuram[2].

From the slopes of the straight lines we calculated the rate constants, $k_s{}^1$ and $k_Q{}^1$. If they are compared to the rate constants for dithiocarbamate formation, $k_{DC}{}^1$, and thiuram disappearance, $k_{TD}{}^1$, according to the measurements of Scheele and Hummel[3], it is quite plain that crosslinking is not tied in with the loss of thiuram, inasmuch as the rate constants $k_s{}^1$ or $k_Q{}^1$ are substantially lower than $k_{TD}{}^1$, whereas they agree quite well with the value for $k_{DC}{}^1$. To be sure, the latter are somewhat larger at all temperatures than $k_s{}^1$ or $k_Q{}^1$, but account must be taken of the fact that the vulcanizates used were
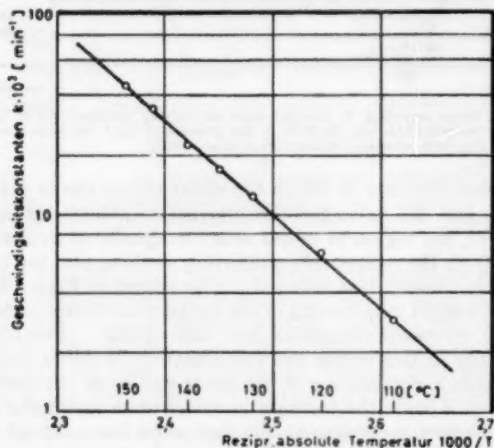
Fig. 7.—Temperature dependence of the rate constants of reciprocal equilibrium swelling and the rise in stress, in the vulcanization of natural rubber with tetraethylthiuram disulfide in the presence of ZnO. Ordinate: rate constants $k \cdot 10^3$ (min^{-1}); abscissa: reciprocal absolute temperature $1000/T$.

cured in a laboratory press, whereas in the study made by Scheele and Hummel this took place in a constant temperature water bath. Thus the differences in the rate constants are doubtless attributable to the fact that the vulcanization temperatures were not exactly the same for each experiment.

Plotting the log of the rate constants against the reciprocal vulcanization temperature, one obtains the straight line shown in Figure 7, from whose slope an activation energy of 22 kcal/mole is computed, in good agreement with the values repeatedly obtained from the temperature dependence of the rate constants for the formation of dithiocarbamate. This is understandable if crosslinking and the rise therewith in stress values are processes which are connected with the dithiocarbamate formation.

Using the comprehensive experimental material assembled by us for thiuram vulcanizations, it can be demonstrated that provided there is a sufficient degree of vulcanization, there exists a linear dependence between reciprocal equilibrium swelling and stress values, the slope of this dependence being a function of the elongation. Evaluation of such relationships has not yet been completed.

Although the details of thiuram vulcanization make for quite a complicated process, our experience and the data assembled with regard to the kinetics of

the process have, we trust, provided a rather lucid picture that should clarify the situation for anyone interested. It has been convincingly demonstrated that neither the diminishing concentration of thiuram disulfide nor the increase in bound sulfur in the vulcanizates are processes that account for the building of bridge bonds, but rather it is the slower process of dithiocarbamate formation to which the crosslinking is related. This is shown by, among other things, the equivalent rates, proved earlier[2] and indicated once again, for dithiocarbamate formation and the change with vulcanization time in the reciprocal equilibrium swelling. That agreement has now also been found, qualitatively as well as quantitatively, between the kinetics of reciprocal equilibrium swelling, and the stress values should, to be sure, not have come as a surprise *per se*; nevertheless it required proper experimental confirmation. It is expected that corresponding relationships could also be derived for reciprocal swelling and other physical properties.

As far as purely thiuram vulcanizations are concerned, it is quite clear which part of the process is decisive for vulcanization: the formation of dithiocarbamate, determinative for the course of crosslinking and for the physical properties as well. In other vulcanization reactions the relationships may not be so simple. For example, kinetic measurements of sulfur vulcanizations accelerated with zinc benzothiazolyl mercaptide bring out the fact that free sulfur disappearance and crosslinking are related phenomena as long as no zinc stearate is present, but that each process displays its own kinetics if the rubber also contains varying amounts of zinc stearate[4]. From this, besides, one can likewise see that the kinetics of the increase in bound sulfur or the diminution of free sulfur is not always of decisive importance for the assessment of the vulcanization process and of the crosslinking.

SUMMARY

As a complement to earlier investigations, and in order to examine more closely the connection between the chemical kinetics and the changes with vulcanization time of the physical properties in the case of vulcanization reactions, we used thiuram vulcanizations as an example, and concerned ourselves with the dependence of stress values (moduli) at different degrees of elongation and different vulcanization temperatures. We found:

1. Stress values attain a limiting value, dependent on the degree of elongation, but independent of the vulcanization temperature at constant elongation.

2. The rise in stress values with the vulcanization time is characterized by an initial delay, which, however, is practically nonexistent at higher temperatures.

3. The kinetics of the increase in stress values with vulcanization time are both qualitatively and quantitatively in accord with the dependence of the reciprocal equilibrium swelling on the vulcanization time; both processes, after a retardation, go according to the first order law and at the same rate.

4. From the temperature dependence of the rate constants of reciprocal equilibrium swelling, as well as of the increase in stress, an activation energy of 22 kcal/mole can be calculated, in good agreement with the activation energy of dithiocarbamate formation in thiuram vulcanizations.

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INVESTIGATION OF RADICAL AND POLAR MECHANISMS IN VULCANIZATION REACTIONS *

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INTRODUCTION

In recent years intensive efforts have been made, with some success, to gain a greater understanding of the vulcanization reaction. W. Scheele and co-workers[1, 2, 3] have analyzed the kinetics of reactant consumption and crosslink formation during the curing process to establish the relative reaction rates. Research work by the British Rubber Producers' Research Association[4, 5, 6, 7] on sulfur-olefin reactions with model compounds has been interpreted to show that these reactions proceed by a polar mechanism. A recent review article[8] discusses and evaluates the findings of a number of authors with a view to clarifying the vulcanization reaction.

Although much is known about the overall vulcanization process, most of the detailed mechanisms are speculative. In view of the wide variety of materials and methods used to effect cure in rubber, it seems reasonable that the reaction can proceed by a variety of mechanisms, dependent on the curing method used. It is our purpose to attempt to establish the free radical or polar character of curing reactions by determining the effect of free radical traps on the rate of crosslinking in styrene-butadiene rubber (SBR) with a variety of curing systems.

EXPERIMENTAL PROCEDURE

Table I lists the compounding formulations (with abbreviations) studied and the sources of the chemicals used. All ingredients were used without further purification. The 1,1-diphenyl-2-picrylhydrazyl (DPPH) was prepared according to the method of Goldschmidt and Renn[9].

A. PREPARATION OF SAMPLES

To avoid the elevated temperatures caused by milling rubber samples, the ingredients were mixed by preparing a gel-free solution of the polymer in benzene and adding the compounding materials in benzene or benzene-acetone solution. All compounding ingredients were weighed to ±0.0001 g and care was taken to adjust comparative formulations (with and without radical traps) within ±0.005 g of each other. Insoluble zinc oxide was suspended in the viscous solution after sieving through a 100-mesh screen. The polymer solution was poured into a shallow tray shaped from 5 mil aluminum sheet and allowed to dry in air, giving films from 0.020 to 0.050 inches thick. During the drying

TABLE I

COMPOSITION OF STOCKS
PARTS PER HUNDRED, BY WEIGHT

Stock Ingredient	Code Name	1	2	3	4	5	6	7	8	10	12	13
SBR 1500[1]		100	100	100	100	100	100	100	100	100	100	100
Zinc oxide		3		3	3	3	3	3	3	3	3	3
Stearic acid		2		2	2	2	2	2	2	2	2	2
Sulfur[2]	S	4		2	2	2	2	2	2	2	2	2
Dicumyl peroxide[3]	DCP		1.2									
Tetramethylthiuram disulfide[4]	TMTD			3								
Diphenylguanidine[5]	DPG				4							
Zinc diethyldithiocarbamate[6]	ZnDETC					1.2						
Benzothiazolyl disulfide[7]	MBTS						0.5	0.5				
"Santocure"[8]									1.2	1.0	1.2	1.0
Mercaptobenzothiazole[5]	MBT											1.0
Hydroquinone[6]	HQ											
Benzoquinone[6]	BQ											
1,5-Di-tert-butylhydroquinone[9]	DTBHQ	Variable										
Quinhydrone[6]	QH											
1,1-Diphenyl-2-picrylhydrazyl	DPPH											
N-Nitrosodiphenylamine[10]	NDPA											

[1] Commercial bale, polymerized at 41° F, contains 1.25 phr N-phenyl-2-naphthylamine, 5.0% rosin acid.
[2] U.S.P. powder, Mallinckrodt Chemical Works.
[3] Recrystallized grade, Hercules Powder Co.
[4] Mathieson Chemical Company.
[5] Eastman Kodak Company.
[6] National Bureau of Standards, standard sample.
[7] Monsanto Chemical Company, "Ethasan O".
[8] Monsanto Chemical Company, N-cyclohexyl-2-benzothiazolylsulfenamide.
[9] Tennessee Eastman Company.
[10] Naugatuck Chemical Company, Retarder J.

procedure the zinc oxide tended to settle somewhat. This concentration differential had no observable effect on the cure except in the TMTD stocks where some nonuniform swelling was noted.

B. CURING AND SWELLING OF SAMPLES

The rubber films were left on the aluminum sheet for support and were cut into $\frac{3}{4}''$ strips. The strips were placed into individual sample tubes in the standard aluminum-block aging apparatus of the type used in this laboratory[10], and were cured by heating in a nitrogen atmosphere. Parallel samples (with and without radical traps) were pulled from the heating block at designated times.

The degree of cure of the samples was determined by volume swelling in benzene. Duplicate strips of rubber for each curing time were covered with benzene in a test tube and allowed to swell for 72 hours at constant temperature (23° C). The period of 72 hours was considered sufficient to allow equilibrium extraction of the sol portion of the rubber. The swollen strips were removed from solution, rapidly blotted dry with filter paper, and weighed in glass-stoppered weighing bottles. The gel content of the rubber was determined by weighing after drying overnight at 80° C in a vacuum oven.

C. CALCULATION OF THE DEGREE OF CROSSLINKING

The modified Flory-Rehner equation[11] was used to determine the effective number of crosslinks, following the method[12] of Adams and Johnson:

$$\nu = \frac{1}{M_c} = -\frac{V_r + \mu V_r{}^2 + \ln (1 - V_r)}{\rho_r V_0 (V_r{}^{\frac{1}{3}} - V_r/2)}$$

ν = effective number of crosslinked units per gram of rubber
M_c = molecular weight between crosslinks
V_r = volume fraction rubber in the swollen vulcanizate
μ = Huggins interaction constant
ρ_r = density of rubber
V_0 = molar volume of the solvent
ρ_s = density of the solvent.

The volume fraction, V_r, was calculated from the reciprocal of the degree of swelling:

$$V_r = \frac{1}{1 + Q}$$

where

$$Q = \left[\frac{\text{weight of solvent in gel}}{\text{weight of gel}} \right] \frac{\rho_r}{\rho_s}$$

The weight of the gel was corrected for the unextractable zinc oxide but no attempt was made to correct for the possibility of other unextracted curing agents in the gel. The values of constants[13] used in the calculations were: $\rho_r = 0.93$ g/cc; $\rho_s = 0.88$ g/cc; $\mu = 0.37$.

RESULTS AND DISCUSSION

The effect of radical scavengers on the crosslinking rate was tested in the following vulcanizing systems:

a. sulfur
b. sulfur-guanidine accelerated
c. sulfur-thiazole accelerated
d. sulfur-sulfenamide accelerated
e. sulfur-thiuram disulfide accelerated
f. sulfur-dithiocarbamate accelerated
g. thiuram disulfide
h. peroxide
i. systems with two accelerators.

The radical scavengers used in the study were benzoquinone, quinhydrone, hydroquinone, 2,5-di-*tert*-butylhydroquinone, 1,1-diphenylpicrylhydrazyl, and N-nitrosodiphenylamine.   The amount of crosslinking (as measured by equilibrium swelling) versus curing time was compared to a parallel sample containing no scavenger.

The unaccelerated sulfur cure (Figure 1) shows a slight increase in the crosslinking rate over the unscavenged stock with hydroquinone, no difference with benzoquinone, and a considerable rate increase with DPPH.   In each case a 2 to 1 mole ratio of scavenger to S_8 concentration was used.   The considerable rate increase in the presence of DPPH can be attributed to an acceleration of the sulfur vulcanization as discussed later and some independent crosslinking by the scavenger.   The lack of effect of HQ or BQ as scavenging agents is in
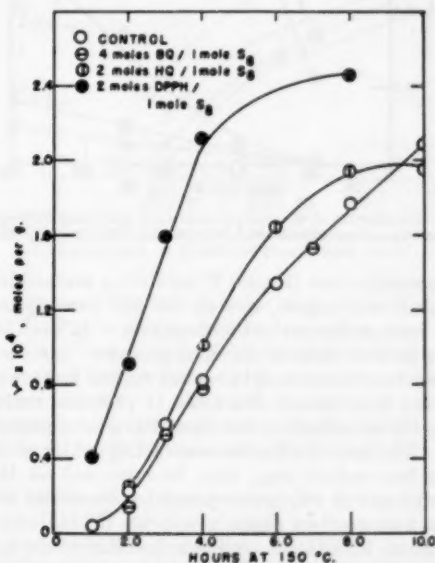
Fig. 1.—Crosslinking of unaccelerated sulfur cures containing benzoquinone, hydroquinone, or 1,1-diphenyl-2-picrylhydrazyl, 150° C.

agreement with the findings of the British Rubber Producers' Research Association that the sulfur-olefin reaction proceeds by a polar chain mechanism[6, 7]. According to Ross[6], known initiators of free radical reactions, such as ultraviolet light and 1,1-a'zobisisobutyronitrile, do not appreciably affect the rate of the sulfur-olefin reaction. He also found that typical inhibitors of free radical chain reactions, such as HQ, failed to retard the reaction. However, organic acids and triethylamine increased the reaction rate. Thus the observed behavior, as illustrated in Figure 1, can be considered to represent a polar mechanism and we will use it as a basis for comparison with the other vulcanizing systems studied.
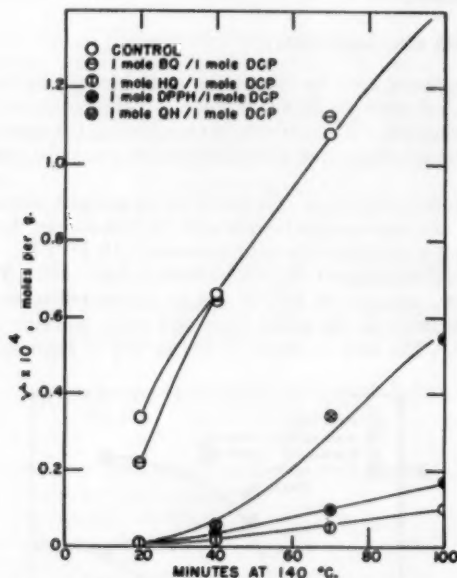
Fig. 2.—Crosslinking of dicumyl peroxide cures containing hydroquinone, quinhydrone, benzoquinone, or 1,1-diphenyl-2-picrylhydrazyl, 140° C.

The dicumyl peroxide cure (Figure 2) exhibits a marked inhibition in crosslinking rate with all scavengers, except for the benzoquinone stock which cures at the same rate as the normal formulation. In each case a ratio of one mole of scavenger to one mole of dicumyl peroxide was used. The dicumyl peroxide-rubber reaction is assumed to be free radical in view of the overwhelming evidence for the free radical character of peroxide reactions. As would then be expected, the crosslinking reaction is almost completely inhibited by HQ and DPPH. The lack of effectiveness of BQ, which is usually considered to be an excellent free radical trap, may be explained on the basis of lesser tendency for RO· to add to BQ as compared to the ability of RO· to abstract hydrogen from the hydrocarbon chain, producing R· radicals. The BQ would be expected to combine with two R· radicals, but this would in effect be creating another crosslink. This interpretation would also explain the intermediate crosslinking rate of the QH-scavenged stock. The observed behavior in Figure

2 can thus be considered to represent a free radical process and we will use it as a basis for comparison in looking for possible evidence of free radical mechanisms in other vulcanizing systems.

Cures by TMTD in the absence of free sulfur were almost completely inhibited by HQ, 2,5-di-*tert*-butylhydroquinone, and QH (Figures 3 and 4). However, because of the complication of a possible reaction between either hydroquinone and TMTD to give the corresponding benzoquinone and dithiocarbamic acid (which would destroy the crosslinking agent), this evidence cannot be considered to be conclusive in favoring a free radical mechanism. However, QH completely inhibits the cure with only one half of the theoretical amount of HQ present for complete reduction of the TMTD. In the presence
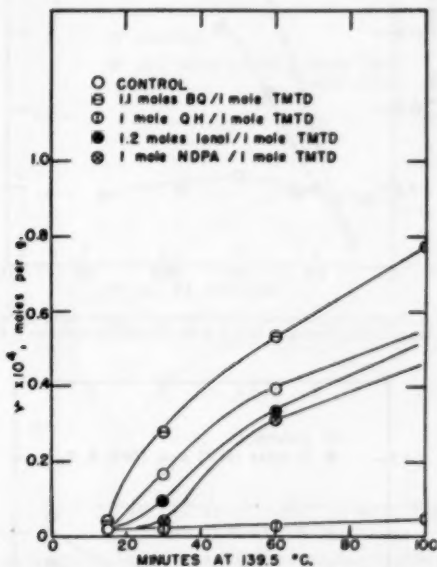
FIG. 3.—Crosslinking of tetramethylthiuram disulfide cures containing benzoquinone, quinhydrone, 2,6-di-*tert*-butyl-p-cresol, or N-nitrosodiphenylamine, 139.5° C.

of DPPH (Figure 4) the TMTD cure is partially inhibited, compared to the catalytic effect of DPPH in the unaccelerated sulfur cure. With 2,6-di-*tert*-butyl-4-methylphenol ("Ionol") and N-nitrosodiphenylamine the TMTD cure is essentially unchanged except for a short induction period. This behavior indicates some initial free radical effect but the ultimate extent of crosslinking is not significantly reduced. Benzoquinone actually contributes to crosslinking in this case, possibly by oxidizing some of the dithiocarbamic acid formed back to TMTD.

Some available information tends to support a free radical character for the vulcanization with TMTD in the absence of free sulfur. Ferington and Tobolsky[14] have demonstrated the ability of TMTD to initiate free radical polymerizations, thus showing that TMTD can cleave homolytically. A possible free radical character is also indicated by the partial inhibition of cure with
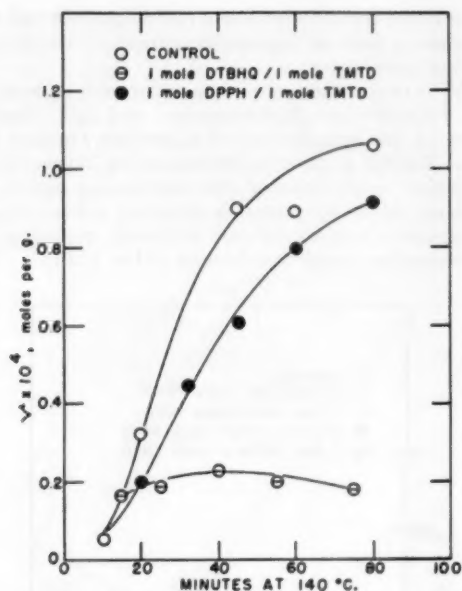
Fig. 4.—Crosslinking of tetramethylthiuram disulfide cures containing 1,1-diphenyl-2-picrylhydrazyl or 2,5-di-*tert*-butylhydroquinone, 140° C.
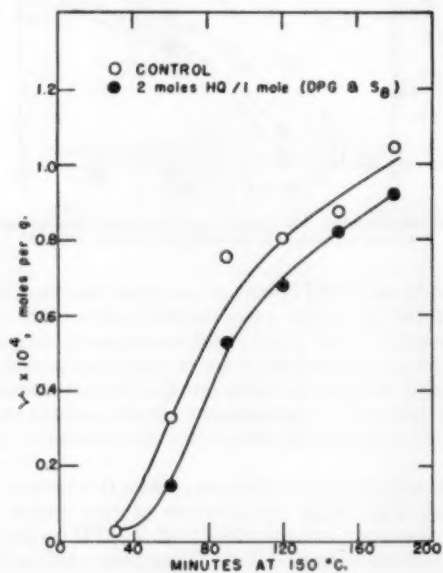
Fig. 5.—Crosslinking of sulfur-diphenylguanidine cures containing hydroquinone, 150° C.

DPPH although the effect is much less than in the case of the peroxide cure. Thus the evidence is not conclusive as to whether the TMTD cure is polar or free radical.

SBR stocks cured with a sulfur-DPG recipe show only a slight induction period with hydroquinone as a radical trap (Figure 5). This indicates that the DPG-catalyzed reaction of sulfur with rubber is a polar reaction. This is in accord with the findings of Krebs[15] who proposes that the opening of an S_8 ring in a polar fashion is greatly facilitated by the presence of an electron pair donor (Lewis base).
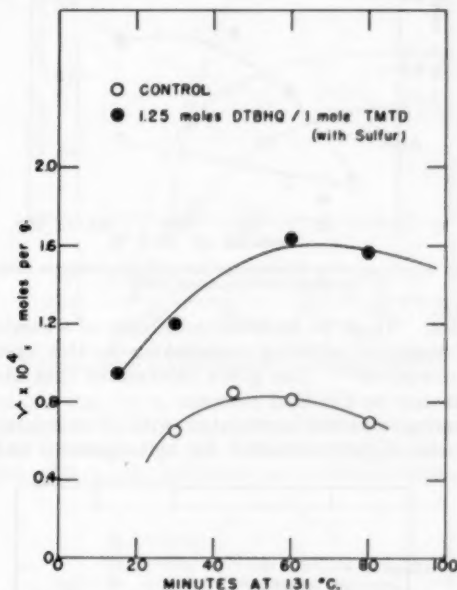
Fig. 6.—Crosslinking of sulfur-tetramethylthiuram disulfide cures containing 2,5-di-*tert*-butylhydroquinone, 131° C.

The use of accelerators of the dithiocarbamate and thiuram disulfide types gave similar results. For example, sulfur curing systems accelerated with TMTD (Figure 6) exhibit an increased amount of crosslinking with hydroquinones in contrast to the TMTD cures in the absence of free sulfur which exhibited a lower amount. The same effect is noted in sulfur systems accelerated with zinc diethyldithiocarbamate (Figure 7) and also with piperidinium-pentamethylenedithiocarbamate when these systems are inhibited with hydroquinones. These results indicate a polar nature in the accelerating effects of dithiocarbamates on sulfur vulcanization of rubber.

When MBTS is used as an accelerator in sulfur curing systems, the crosslinking is somewhat retarded by HQ, 2,5-di-*tert*-butylhydroquinone, and BQ (Figures 8 and 9). The crosslinking was notably accelerated by DPPH in a concentration sufficient to scavenge all of the MBTS and the $\cdot S_2 \cdot$ biradicals that might be formed. This behavior is good evidence for a polar mechanism. The retarding effect of the other materials suggests the possible presence of a
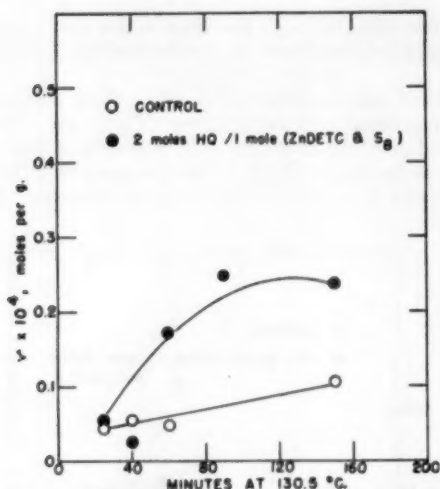
Fig. 7.—Crosslinking of sulfur-zinc diethyldithiocarbamate cures containing hydroquinone, 130.5° C.

free radical reaction. Thus, we have the possibility of a combination of polar and free radical reactions effecting crosslinking in this system. Work by Dogadkin and coworkers[16, 17] has given indications that the sulfur-MBTS reaction in rubber may be a radical process.

The sulfur curing systems accelerated with N-cyclohexylbenzothiazolyl sulfenamide are also slightly retarded by hydroquinone and benzoquinone
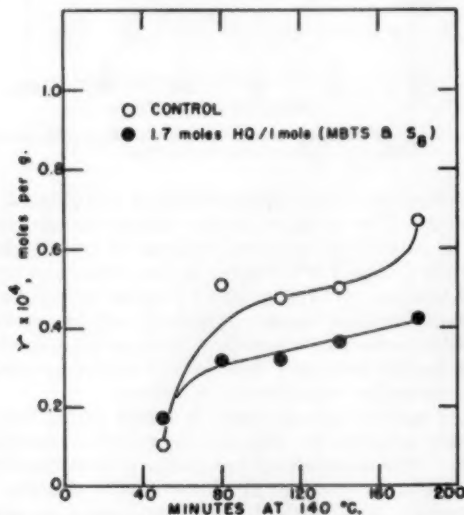
Fig. 8.—Crosslinking of sulfur-benzothiazolyl disulfide cures containing hydroquinone, 140° C.
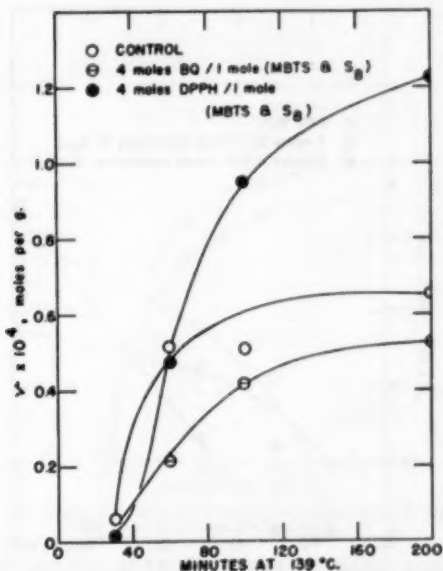
Fig. 9.—Crosslinking of sulfur-benzothiazolyl disulfide cures containing benzoquinone or 1,1-diphenyl-2-picrylhydrazyl, 139° C.

(Figures 10 and 11) but, as in the case of MBTS, a considerable amount of crosslinking still occurs. Cures containing DPPH in a concentration theoretically sufficient to scavenge all of the accelerator and $\cdot S_2 \cdot$ biradicals that could be formed exhibit a 30-minute induction period before starting to cure at a rate
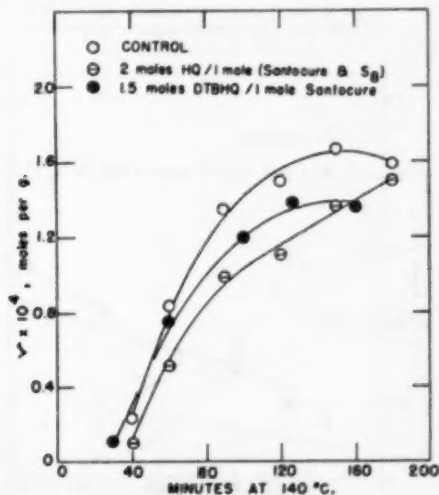
Fig. 10.—Crosslinking of sulfur-Santocure cures containing hydroquinone or 2,5-di-tert-butylhydroquinone, 140° C.
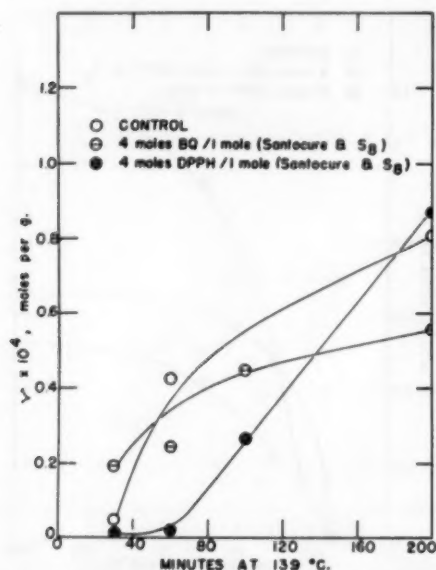
Fig. 11.—Crosslinking of sulfur-Santocure cures containing benzoquinone or 1,1-diphenyl-2-picrylhydrazyl, 139° C.

initially comparable to the unscavenged stock. This again seems to indicate the possibility of both radical and polar processes occurring simultaneously to effect crosslinking. Dogadkin and coworkers[18] have found that N,N-diethyl-2-benzothiazolyl sulfenamide has a structure-forming effect when heated in
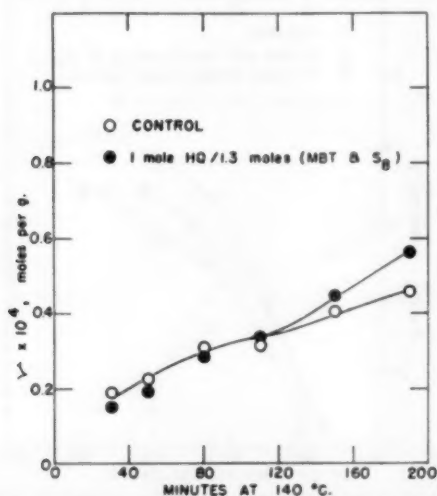
Fig. 12.—Crosslinking of sulfur-mercaptobenzothiazole cures containing hydroquinone, 140° C.
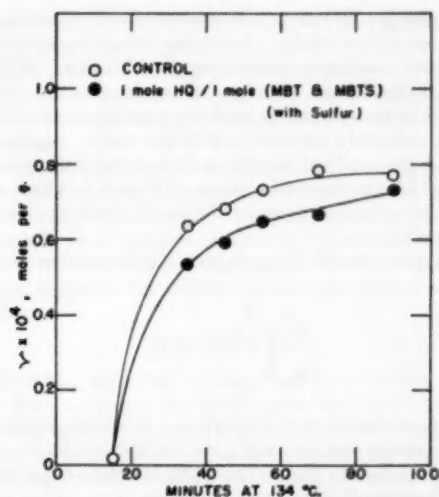
Fig. 13.—Crosslinking of sulfur-mercaptobenzothiazole-benzothiazolyl disulfide cures containing hydroquinone, 134° C.

SBR without free sulfur.   After extraction the stocks contained chemically combined sulfur and nitrogen.   The structure-forming effect of the sulfenamide was considered to be equivalent to free radical polymerization.

Sulfur cures accelerated with mercaptobenzothiazole alone (Figure 12) are
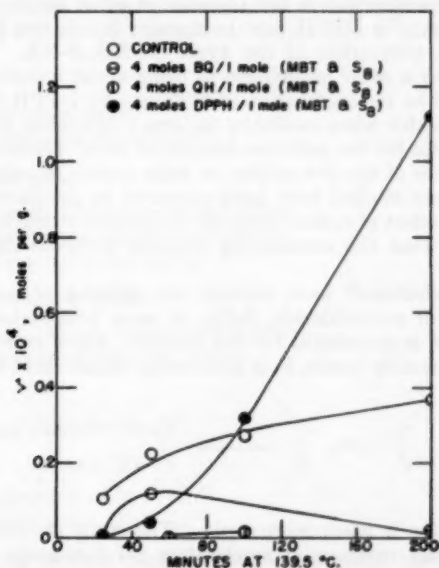
Fig. 14.—Crosslinking of sulfur-mercaptobenzothiazole cures containing benzoquinone, quinhydrone, or 1,1-diphenyl-2-picrylhydrazyl, 139.5° C.

only slightly affected by HQ or 2,5-di-*tert*-butylhydroquinone, whether in the presence or absence of zinc oxide.   A similar effect in sulfur cures was noted with two-accelerator mixtures containing MBT (e.g., MBT-DPG, MBT-TMTD, MBT-MBTS) in the presence of hydroquinone (Figure 13).   The presence of DPPH initially retards and then accelerates curing rate (Figure 14).   BQ and QH definitely interfered with the cure.   Again we find evidence for both polar and free radical reactions but the qualitative relationships in Figures 12, 13, and 14 are more like those of Figure 1 which represent a polar mechanism than they are like those of Figure 2 which are known to involve a free radical mechanism.

Dogadkin and coworkers[19, 20] postulate the formation of the intermediate polysulfide,
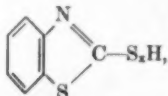
which then decomposes to effect crosslinking.   While they propose a free radical mechanism, our findings and the work of the British Rubber Producers' Research Association relative to the sulfur-olefin reaction suggest that a polar decomposition of the polysulfide is more probable.

Armstrong, Little, and Doak[21] have suggested that the sulfur-MBT-rubber reaction is free radical since this reaction is inhibited by oxygen.

The known free radical DPPH functioned as an efficient free radical trap only in the peroxide curing system.   In all the formulations containing free sulfur this material consistently accelerated the crosslinking reaction either immediately, as in the case of the unaccelerated sulfur cure, or after a short induction period as observed in the presence of other accelerators.   This behavior suggests that the DPPH may be opening the S_8 ring by a free radical attack to form a polysulfide of the type, $RNS-S_x-S-NR$.   The polysulfide could then react by a polar mechanism to bring about crosslinking.   Another explanation would be the abstraction of hydrogen by DPPH from the rubber, or from the accelerator when available, to form a hydrazine which would then act as an accelerator for the polar mechanism of sulfur vulcanization.

Some indications of the free radical or polar nature of vulcanizing systems other than the ones studied here have appeared in the literature.   Turner[22] has measured the effect of radical traps on the radiation crosslinking of rubber. His results show that the crosslinking reaction proceeds through a radical mechanism.

Glazer and Schulman[23] have studied the gelation of natural rubber in benzene with sulfur monochloride, S_2Cl_2, at room temperature.   Although a radical mechanism is postulated for the reaction, which crosslinks by adding sulfur across two double bonds, it is interesting to note that in the more polar

solvents the gelation is much more rapid.   The study showed that in rubber solutions containing commercial accelerators gel formation for accelerators containing ionic groups or available electron pairs, e.g. zinc isopropylxanthate,

diethylammonium diethyldithiocarbamate, MBT, and aniline, was much more rapid than for the less polar accelerators, MBTS and N-cyclohexyl benzo-thiazolylsulfenamide.   These findings, assuming sulfuration with sulfur mono-chloride to be polar, are in accord with our work which indicates that the sulfur-olefin reaction is more polar in the presence of the former accelerators than with the latter accelerators.

The faster curing rate of natural rubber and other *cis*-polyisoprenes com-pared to styrene-butadiene copolymers may be attributed to enhancement of the polarity of the double bond by the adjacent methyl group.   The increased electron density would thus increase the reactivity toward a positive attacking group such as $R\text{-}S_x^+$.   The effect of carbon blacks of different pH on the rate of sulfur cures also supports the interpretation that sulfur cures involve polar reaction mechanisms.

CONCLUSIONS

The results obtained with free radical traps in a variety of curing systems for SBR rubber give evidence for both polar and free radical mechanisms. There is apparently no one mechanism even for sulfur vulcanization and the relative free radical or polar character of the crosslinking reaction varies over a broad range including situations in which both types occur in the same formu-lation.   This may be due to competing reactions which function independently, or it may be the result of a combination of polar and free radical reactions in a single complex mechanism.   For example, certain accelerators may initiate the reaction by dissociation to free radicals which attack the S_8 molecule and form polysulfides which then decompose by a polar mechanism to initiate the prop-agation stage of the reaction.

Based on the information obtained in this study and other supporting evidences, it is possible to group the familiar curing systems according to the apparent polar or free radical character of the reaction as observed in SBR.

Polar:

> unaccelerated sulfur
> guanidine-accelerated sulfur

Predominantly polar:

> thiuram disulfide-accelerated sulfur
> dithiocarbamate-accelerated sulfur
> thiazole-accelerated sulfur

Mixed polar and free radical:

> thiazole disulfide-accelerated sulfur
> sulfenamide-accelerated sulfur

Inconclusive:

> thiuram disulfide cure

Free radical:

> peroxide cure
> radiation cure

It is interesting to note that the accelerated sulfur curing systems which most closely approximate a polar mechanism either involve an amine (DPG) or

a compound which is either present as a zinc salt (dithiocarbamate) or can easily form zinc salts at the curing temperature (thiuram disulfide and mercaptobenzothiazole systems). All curing systems studied which include free sulfur appear to involve a polar mechanism.

ACKNOWLEDGMENT

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DERIVATIVES OF 2-MERCAPTOBENZOTHIAZOLE
AS ACCELERATORS *

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The wide use in industry of new types of synthetic rubbers calls for the creation of a variety of vulcanization systems of specific action. The quest for such vulcanization systems and, in particular, for vulcanization accelerators with given properties is of course made more difficult by the fact that up to the present time no one has cleared up the question of the influence of the chemical structure of the accelerators upon their vulcanizing activity. As a result of this the provision of experimental data revealing the connection between the chemical structure and the action of vulcanization accelerators is of immediate theoretical and practical value.

The work to be described concerns the investigation of the vulcanization activity of a series of sulfenamide derivatives of 2-mercaptobenzothiazole (MBT), differing in chemical structure, of the general formula

$$C_6H_4 \underset{S}{\overset{N}{\diagdown}} C-S-N \ (RR_1)$$
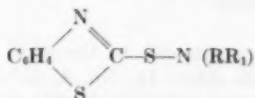
where R and R_1 are alkyl, aryl, azine and other radicals. We investigated the following compounds: N,N-diethyl-2-benzothiazolylsulfenamide, N-oxydiethylene-2-benzothiazolylsulfenamide, N-cyclohexyl-2-benzothiazolylsulfenamide, N,N-dicyclohexyl-2-benzothiazolylsulfenamide, and N-phenyl-2-benzothiazolylsulfenamide.

The vulcanizing activity of these compounds was assessed by their action in unfilled SBR rubber stocks from data of the kinetics of combination of sulfur and the degree of crosslinking (from the swelling maximum) at vulcanization temperature 143°. The compounds investigated as vulcanization accelerators were added in equimolecular amounts in relation to 1.0 part by weight of N,N-diethyl-2-benzothiazolylsulfenamide (Sulfenamide BT), widely used in industry at the present time as an accelerator.

It had already been established[1,2] that the kinetics of vulcanization of rubber in the presence of sulfenamide derivatives of MBT is marked by the presence of an induction period. The experimental data set forth below are evidence that the length of the induction period of vulcanization is to a considerable extent determined by the type of radicals attached to the amine group.

The data given in Figure 1 show that with the use of N-oxydiethylene-2-benzothiazolylsulfenamide (Curve 3) the induction period is more prominent than in the case of N-cyclohexyl- and N,N-diethyl-2-benzothiazolylsulfenamide

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(Curves *2* and *1*). A considerable increase in the duration of the induction period is observed when we change over from N-cyclohexyl-2-benzothiazoyl-sulfenamide   (Curve *2*)   to   N,N-dicyclohexyl-2-benzothiazolylsulfenamide (Curve *4*).   Weakening of the vulcanizing activity takes place also if we replace the cyclohexyl by a phenyl radical.

Thus the data presented show that by the addition to the amino group of benzothiazoylsulfenamide radicals of varying structure it is possible to obtain accelerators differing considerably from each other in their vulcanizing activity, and in particular, in the duration of their induction period.

Fig. 1.—Influence of sulfenamide derivatives of MBT upon the kinetics of combination of sulfur in the vulcanisation of unfilled stocks of SBR rubber (SKS-30A): *1*—N,N-diethyl-2-benzothiazolylsulfenamide; *2*—N-cyclohexyl-2-benzothiazolylsulfenamide; *3*—N-oxydiethylene-2-benzothiazolylsulfenamide; *4*—N,N-dicyclohexyl-2-benzothiazolylsulfenamide.

Considerable importance attaches to the state of affairs which we have already found, (see *Kolloid. Zhur.* **21**, No. 4, 427–35 (1959), RJM) that on changing over from sulfenamide compounds with the characteristic

$$-S-N-$$

group to compounds containing

$$-S-C-N-$$

we observe a marked acceleration of vulcanization in the initial stage of this process.   As may be seen from Figure 2, the rate of vulcanization in the presence of diethylaminomethyl-2-thiolbenzothiazole

is considerably higher than when N,N-diethyl-2-benzothiazolylsulfenamide

Fig. 2.—Vulcanization activity of sulfenamide and aminomethyl derivatives of MBT (in unfilled SKS-30A stocks). 1—N,N-diethyl-2-benzothiazoylsulfenamide; 2—diethylaminomethyl-2-thiobenzothiazole; 3—oxydiethylene aminomethyl-2-thiobenzothiazole; 4—N-oxydiethylene-2-benzothiazoylsulfenamide.

is used. An analogous state of affairs is observed when we compare N-oxydiethylene-2-benzothiazolylsulfenamide
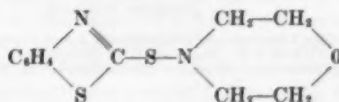
with the corresponding aminomethyl derivative
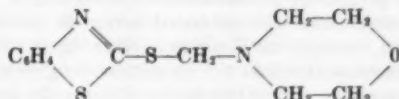
The data in Figure 2 on the alteration in the swelling maximum show that in the presence of aminomethyl derivatives of MBT crosslinking occurs at an earlier stage of the vulcanization process than with the sulfenamide compounds. Thus, for instance, a stock containing N,N-diethyl-2-benzothiazolylsulfenamide, after 10 min heating at a vulcanization temperature of 143°, continues to swell indefinitely in xylene, while diethylaminomethyl-2-thiolbenzothiazole even as a result of 5 min vulcanization leads to a crosslinked vulcanizate.

TABLE 1

PER CENT OF DIETHYLAMINOMETHYL-2-THIOLBENZOTHIAZOLE (A) AND N-CYCLOHEXYL-2-BENZOTHIAZOLYLSULFENAMIDE (B) WITH MBTS TAGGED WITH S^{35}

Vulcanization accelerator	Temperature, ° C				
	30		60	80	100
			Time, hours		
	2.5	18	2	2	2
A	13.7	94	98	100	—
B	—	0	0	96	100

The enhanced vulcanizing activity of the aminomethyl derivatives of MBT is connected with the greater ease of decomposition of these derivatives into free radicals, which is indicated by the data[3] of isotope exchange of aminomethyl and sulfenamide compounds with 2-benzothiazolyl disulfide (MBTS) tagged with S^{35} as shown by the data of Table 1.

The exchange of benzothiazolyl radicals between diethylaminomethyl-2-benzothiazole and 2-benzothiazolyl disulfide takes place at a lower temperature than in the N-cyclohexyl-2-benzothiazolylsulfenamide—2-benzothiazolyl disulfide system.

The possibility of adjusting the dynamics of vulcanization by using appropriate accelerators has great practical significance.
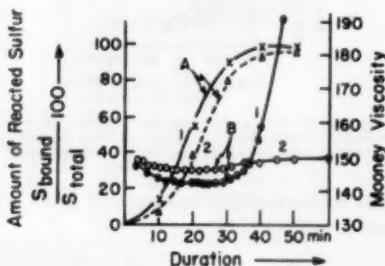
FIG. 3.—Action of N,N-diethyl-2-benzothiazolylsulfenamide *1* and N-oxydiethylene-2-benzothiazolyl-sulfenamide *2* in tread stocks of SKS-30 AM, containing HAF carbon-black. A—kinetics of combination of sulfur at vulcanization temperature 143°; B—dynamics of alteration in Mooney viscosity at 115°.

In recent years 'high-dispersity' furnace blacks have been used in industry, and their presence in vulcanization stocks raises the rate of vulcanization and increases the risk of premature vulcanization ('scorching'). The employment in such stocks of accelerators with retarded action in the initial stage of the process and increased intensity in the stage following enables us to eliminate premature vulcanization without at the same time lengthening the time taken to reach the optimum cure. From this point of view, the accelerator N-oxydiethylene-2-benzothiazolylsulfenamide, whether in rate of combination of sulfur (Figure 3 A) or in the rate of alteration in viscosity at 115° (Figure 3 B), has an undoubted superiority over N,N-diethyl-2-benzothiazolylsulfenamide. The demonstrated kinetics of vulcanization has a favorable influence both on the bond strength of multiply vulcanized rubber articles[4] and upon the endurance of vulcanizates under repeated deformations[1].

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VULCANIZATION OF RUBBER IN THE PRESENCE OF N,N-DIETHYL-2-BENZOTHIAZOLYLSULFENAMIDE AS ACCELERATOR

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In the presence of the majority of accelerators the kinetics of vulcanization may be described by a first order equation. However, in the work of Dogadkin and coworkers[1], Zapp[2], and others, it has been established that in several systems there is an initial period in which the rate of vulcanization is retarded. This initial period (called an induction period) is most clearly seen with sulfenamide accelerators such as N,N-diethyl-2-benzothiazolylsulfenamide (marketed as a vulcanization accelerator in the USSR under the brand name of "Sulfenamide BT" and in Germany under the brand name of "Vulkacit AZ"). Possessing an ability to retard vulcanization in the earlier phases, these accelerators provide a high rate of vulcanization in the later phases of the process.

The presence of an induction period aids in prolonging the period in which the compounds are in the plastic state, thus improving the properties of the many articles manufactured from rubber and creating the conditions in which the vulcanization molds will be well filled, and so forth. Accelerators which provide a similar form of vulcanization kinetics have therefore found the greatest development. The latter circumstance impelled us to study the peculiarities of vulcanization in the presence of sulfenamide accelerators, the action of which is not completely elucidated in the literature.

The investigations of sulfenamide accelerators were conducted by us on unfilled compounds of sodium-butadiene rubber prepared by the following recipe in parts per hundred of rubber (phr) by weight: rubber-100, sulfur-2.0, Sulfenamide BT-1.0, zinc oxide-5.0, stearic acid-2.0, Neozone D (PBNA)-2.0. Depending on the purpose of the experiment certain changes were made in the compound recipe. The compounds were prepared on a micromill and vulcanized in an electropress at 143°.

The bound sulfur was determined in the vulcanizates by the method of oxidation by nitric acid with bromine in the presence of magnesium oxide and radiometrically. The number of crosslinks was calculated from the equation of Flory and Rehner[3] from maximum swelling values in xylene.

The kinetics of sulfur addition and the formation of crosslink chains.—The kinetics of the addition of sulfur to rubber, as has already been noted, is characterized by an S-shaped curve (Figure 1, Curve *1*), so that in the process of vulcanization with Sulfenamide BT it is possible to distinguish three periods: the initial (induction) period, during which the rate of vulcanization is small; the main period, during which the sulfur adds to the rubber with some constant rate substantially greater than that of the initial period, and, finally, the period
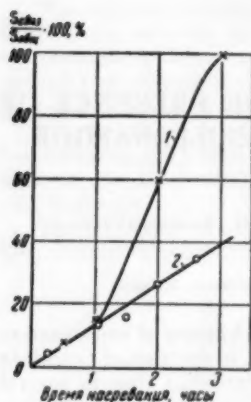
Fig. 1.

Fig. 2.

Fig. 1.—The kinetics of the addition of sulfur in compounds with Sulfenamide BT.
1—with accelerator; 2—without accelerator.
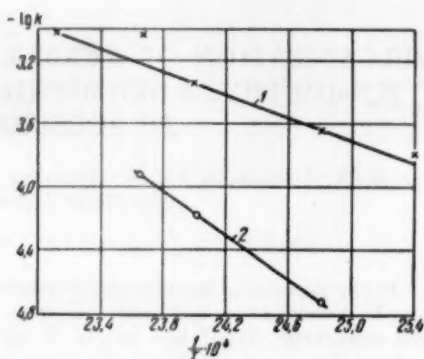
Fig. 2.—The dependence of the rate constant for the addition of sulfur on the temperature of
vulcanization. 1—in the stationary period; 2—in the initial period.

during which the reaction terminates. The rate of addition of sulfur to rubber
in the initial period is approximately the same as that observed in the vulcaniza-
tion of the same compound without accelerator (Figure 1), i.e., during the in-
duction period the Sulfenamide BT acts as if it exerts no influence on the rate of
addition of sulfur to the rubber. This conclusion is also confirmed from the
value of the activation energy calculated for the addition reaction of sulfur to
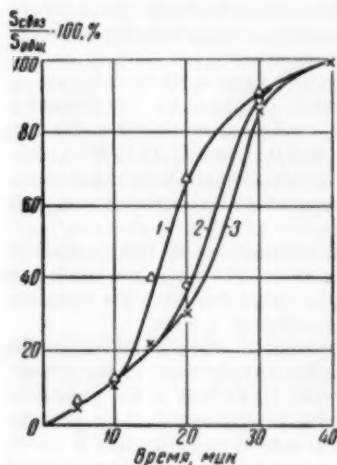
Fig. 3.

Fig. 4.

Fig. 3.—The influence of concentration on the addition of sulfur to rubber.
1—3.0%; 2—2.0%; 3—1.0% S.
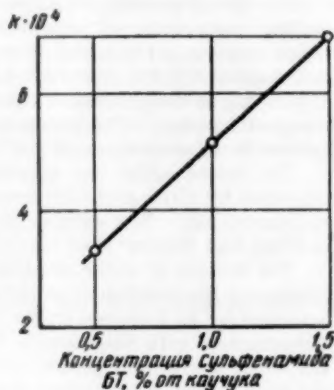
Fig. 4.—The dependence of the rate constant for the addition of sulfur to rubber in
the main period on the concentration of Sulfenamide BT.

rubber during the induction period. This activation energy, which equals 30 kcal/mole, coincides with the activation energy of the addition of sulfur to rubber in the absence of accelerator[4] and matches the energy required to open the eight membered sulfur ring. During the main period, the energy of activation for the addition of sulfur to rubber is equal to 14 kcal/mole which indicates that the accelerator, or more correctly, its decomposition products, take an active part in the addition of sulfur to rubber during this period.

The activation energy was calculated from the slope of the kinetic plots in the temperature interval between 120° and 160° (Figure 2). The rate of addition of sulfur to the rubber during the main period, expressed as a ratio between the bound sulfur and the total sulfur, depended both on the initial concentration of the sulfur in the rubber (Figure 3) and on the concentration of accelerator. In the latter case this dependence was linear (Figure 4).
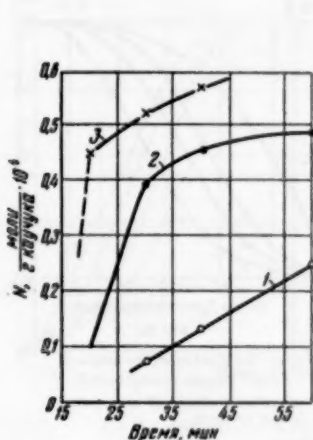
Fig. 5.—The kinetics of the formation of crosslink chains for compounds with various concentrations of total sulfur. 1—1.0% S; 2—2.0% S; 3—3.0% S. N is the number of crosslinks.
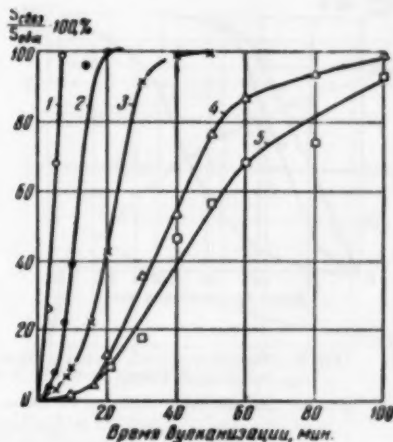
Fig. 6.—The influence of temperature on the kinetics of the addition of sulfur in the presence of Sulfenamide BT. 1—160°; 2—150°; 3—143°; 4—130°; 5—102°.

The formation of a three dimensional structure in vulcanizates of compounds with Sulfenamide BT is also characterized by a prolonged induction period. After 15 to 40 minutes of heating, a single three dimensional structure is formed with a concentration of crosslinks in the order of 0.1 to 0.4×10^{-4} mole/gram of rubber (Figure 5). This is the point at which the amount of sulfur added to the rubber is greater than 40 per cent of that introduced. The formation of a three dimensional structure after an induction period occurs at a high rate and, upon the attainment of the optimum cure, the number of crosslinks is insignificantly changed. Upon raising the temperature of vulcanization, the duration of induction period decreases and at 160° the induction period is practically absent in the rate curve (Figure 6).

The influence of the alkalinity of the rubber.—Industrial sodium-butadiene rubber (SKB) contains a residue of a basic nature and the most clear induction period appears when such rubber is purified to remove the alkali. The rate

curve of the addition of sulfur to SKB compounds which contain a small concentration of alkali (less than 0.1 per cent calculated as Na_2CO_3) have the characteristic S-shaped form with a long induction period (Figure 7). A single three dimensional structure in the vulcanizate is formed only after 30 minutes of vulcanization. At a greater alkali content in the compound ($\geqslant 0.75$ per cent) the induction period in the kinetic curve vanishes. This influence of alkali may be explained by its well known acceleration action on the process of vulcanization.

The influence of oxygen.—It may be hypothesized that the initial period of the inhibited addition of sulfur is connected with the presence in the medium of oxygen and oxygen containing compounds which react with the accelerator or radicals which are formed from the accelerator. A similar inhibiting action of
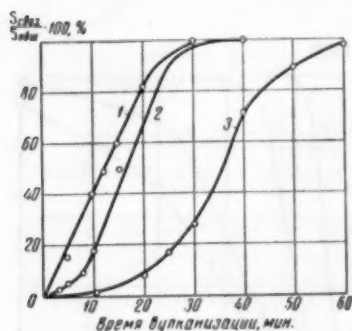
FIG. 7.—The influence of the content of alkali in the rubber on the kinetics of the addition of sulfur. *1*—0.75%; *2*—0.37%; *3*—0.1% alkali.
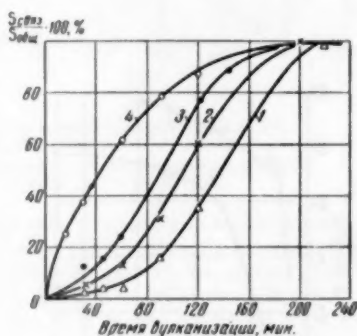
FIG. 8.—The influence of oxygen on the addition of sulfur to rubber (vulcanized in ampules). *1*—0.2%; *2*—4.7%; *3*—21%; *4*—100% O_2 (by volume).

oxygen on the addition of sulfur was noted by Bloomfield[4]. In order that this possibility might be proved or disproved, vulcanization was conducted both in the absence of oxygen and in the presence of determined amounts of oxygen. Vulcanization was carried out by two methods: by heating the compound in ampules and in a press. In the first case, compounds were prepared from an alkali free rubber on a micromill encased in a specially constructed cabinet filled with nitrogen or argon[5]. The ingredients (accelerator, sulfur and zinc oxide) were first placed in a vacuum and then saturated with nitrogen. Samples of the compound were then placed in ampules containing either pure nitrogen or a mixture of nitrogen and the required quantity of oxygen, and the ampules heated in an oil thermostat. In the second case the samples were prepared on a micromill in a cabinet filled with a gaseous mixture of nitrogen containing a specified concentration of oxygen. The samples were packaged in cellophane packets in the same atmosphere and placed in the vulcanization molds which were then heated in an electropress.

As may be seen in Figure 8, which presents the results of the work in ampules, the greatest induction period was observed in the case of vulcanization in an atmosphere of nitrogen containing not more than 0.2 per cent oxygen; as the concentration of oxygen increases in the reaction, the size of the induc-

tion period diminishes.   During vulcanization in the presence of pure oxygen, the induction period vanishes and the S-shaped kinetic curve of the addition of sulfur transforms to one that is convex toward the axis of the concentration of added sulfur.   Analogous results were obtained from vulcanization in a press. However, due to the smaller absolute concentration of oxygen in the vulcanizates, the influence of the oxygen is less apparent, although the kinetic curves fall in the same order as those in the experiments in which the compounds were heated in ampules.   Thus in the presence of Sulfenamide BT, oxygen accelerates the addition of sulfur to rubber and cannot be the cause of the induction period.

The acceleration of the sulfur addition reaction in rubber by the molecular oxygen may be explained by the formation during oxidation of the rubber of polymer radicals which are free to react with sulfur.   Besides this, peroxy com-
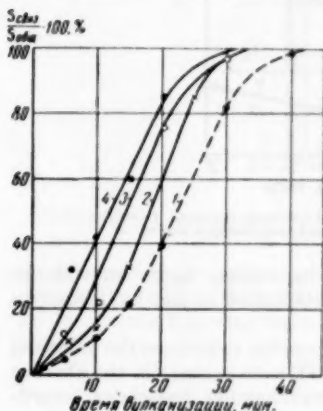
Fig. 9.—The influence of cumene hydroperoxide on the kinetics of sulfur addition.
    1—0%; *2*—0.5%; *3*—1% peroxide.
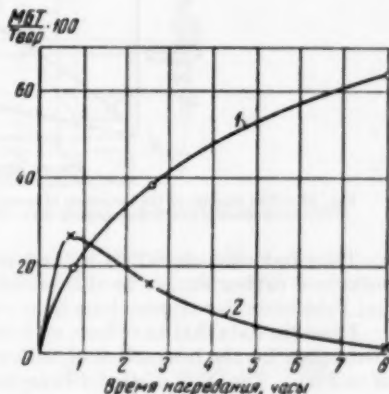
Fig. 10.—The kinetics of the addition of benzothiazolyl thiyl radicals to rubber (from bound sulfur) in a system of rubber +6 wt. % Sulfenamide BT.   *1*—content of bound benzothiazolyl thiyl radicals; *2*—content of free mercaptobenzothiazol.

pounds, which are formed in the oxidation of rubber, apparently form an oxidation-reduction system with the Sulfenamide BT with the result that there occurs a more intense formation of accelerator radicals.

Actually, as may be seen in Figure 9, cumyl hydroperoxide, to a substantial degree, increases the rate of the addition of sulfur to rubber in the presence of Sulfenamide BT.   The possibility of the activation of the elemental sulfur by active forms of oxygen containing compounds is not excluded.

The interaction of N,N-diethyl-2-benzothiazolylsulfenamide with rubber.— The vulcanization process is accompanied by the addition to the rubber of the elements of the accelerator and the formation of MBT (mercaptobenzothiazole) and diethylamine.   MBT can be isolated from the acetone extract of the vulcanizate and quantitatively determined by titrating with a solution of copper oleate.   The presence of free diethylamine is determined by a qualitative reaction with sulfur dioxide and copper sulfate.

In Figure 10 are presented the kinetics of the addition of the elements of the accelerator (based on the bound sulfur) to the rubber at 143° (the compound

contained 6 phr of Sulfenamide).   Curve *2* on the same graph shows the accumulation of free MBT.   A maximum is observed which may be assumed to result from the subsequent transformation of the MBT into its diethylamine salt.   The interaction of Sulfenamide BT with rubber (in the absence of sulfur) is accompanied by a loss of solubility by the rubber, a decrease in the plasticity and an increase in the elasticity, i.e., there appears all the indications of vulcanization.   The number of chemical crosslinks in compounds of the sodium-butadiene rubber with 6 phr of Sulfenamide BT increases with the degree of heating substantially faster than that observed by heating the rubber alone (Figure 11).

Fig. 11.—The kinetics of the formation of crosslinks in the following systems. *1*—rubber; *2*—
rubber plus 6% Sulfenamide BT. *N* is the number of crosslink chains.

Thus Sulfenamide BT is an independent vulcanizing agent for sodium-butadiene rubber similar to that which was established earlier by Dogadkin and Feldshtein[1] for styrene-butadiene rubber.

From the data that have been set forth, it is possible to propose the following mechanism for the interaction of Sulfenamide BT with rubber (in the absence of sulfur).   The N,N-diethyl-2-benzothiazolylsulfenamide dissociates according to the following equation.

$$\tag{1}$$

The radicals $(Y\cdot)$, formed by the splitting of the accelerator, in a manner similar to the radicals, formed by the decomposition of MBTS (benzothiazolyldisulfide)[6], exert a structurizing influence on the rubber, interacting with it in two ways:

a) Addition at the double bond:

$$-CH_2CH{=}CHCH_2- \;+\; Y\cdot \longrightarrow -CH_2CHYCHCH_2- \tag{2}$$

b) Abstraction of hydrogen from the α-methylene group (or hydrogen from the *tertiary* carbon atom† of the structure $2-1$):

$$-CH_2CH{=}CHCH_2- \;+\; Y\cdot \longrightarrow -\,\dot{C}HCH{=}CHCH_2- \;+\; YH \tag{3}$$

where YH is MBT or diethylamine.

† Presumably the author means hydrogen from the *tert.* carbon arising from 1,2 polymerization.   (Ed.).

The presence of the first process is confirmed by the detection of chemically bound sulfur and nitrogen in the rubber, and the second, by the formation of MBT and diethylamine in the vulcanizate.

The radicals which emerge from the polymer interact with themselves or with the double bond of other rubber molecules and, in agreement with the scheme proposed by Dogadkin[5], form the crosslinked —C—C— three dimen-
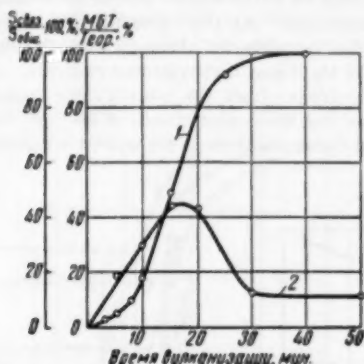
FIG. 12.—1—Kinetics of the addition of sulfur; 2—content of free MBT in the compound.

sional structure of vulcanizates. The reaction between rubber (RuH) and N,N-diethyl-2-benzothiazolylsulfenamide might also be presented as a bimolecular process following the scheme:
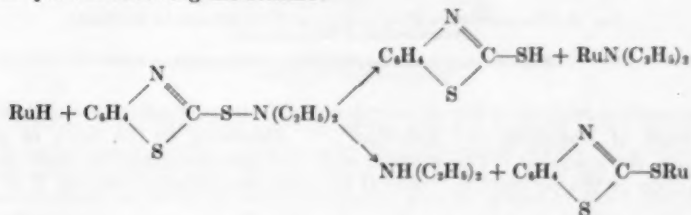
However, such a hypothesis is not substantiated by kinetic data and does not explain the structurization (vulcanization) of the rubber by the Sulfenamide BT (without sulfur).

The mechanism of the action of Sulfenamide BT as a vulcanization accelerator.— In the presence of sulfur and activator (compounds containing 2 phr sulfur, 1 phr Sulfenamide BT, 5 phr zinc oxide and 2 phr stearic acid) the decomposition of the accelerator was of like character as was found in the binary mixture of rubber and accelerator.

Figure 12 presents the kinetics of the addition of sulfur to rubber and the formation of MBT during the vulcanization of the above mentioned industrial compound.

Figure 13 depicts the kinetics of the accumulation of bound nitrogen in the vulcanizates due to the addition of the accelerator radicals to the rubber. The quantity of radicals that are incorporated reaches 60 per cent of the accelerator that was introduced (about 1 per cent based on rubber).

The formation of free diethylamine in the vulcanized compound containing 10 phr sulfur, 10 phr Sulfenamide BT and 2 phr zinc stearate, is shown in Figure 14. In this case the compound was heated in mineral oil and the diethylamine which is formed during the interaction of the accelerator with the rubber distilled out of the reaction area with nitrogen.

On the basis of the experimental data that have been obtained, the following mechanism for the action of Sulfenamide BT as an accelerator for sulfur vulcanization may be presented. At the vulcanization temperatures of 140° to 160° there occurs, as has been shown above, a dissociation of the Sulfenamide BT into benzothiazolyl thiyl and diethylamine radicals. Interacting with the rubber, they extract hydrogen from the α-methylene group (or the third atom of the 1–2 structure) of the molecular chains of rubber, forming MBT and diethylamine. Mercaptobenzothiazole is an active accelerator and enters into
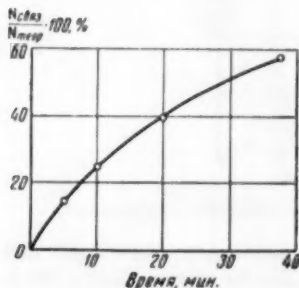
Fig. 13.

Fig. 14.

Fig. 13.—The dependence of the quantity of bound nitrogen on the time of vulcanization of the compound.
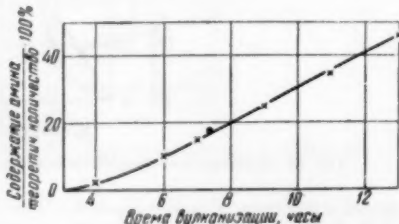
Fig. 14.—Kinetics of the formation of diethylamine at 143°.

an interaction with the sulfur in accordance with the mechanism brought out by the work of Dogadkin and Tutorskiĭ[8–10]. According to the work of these authors, the reactions between sulfur and mercaptobenzothiazole leads to the formation of the polysulfide biradical $S_x\cdot\cdot$, the persulfhydryl radical $\cdot S_x H$ and
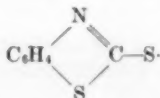
the benzothiazolyl thiyl radical which add to the rubber. The important role of the MBT in the reaction with sulfur is seen in Figure 12; the curve characterizing the accumulation of MBT in the compound has a maximum which correlates with the maximum rate of the addition of sulfur to the rubber. The decrease in the content of free MBT observed beyond the maximum is explained in this case by the addition of it to the rubber which, as was established by Dogadkin and Tutorskiĭ[8], occurs as long as there is free sulfur in the compound. An analogous action may be assumed for the acceleration role of diethylamine. However, the participation of diethylamine in vulcanization is apparently small (in comparison to that of MBT) since there occurs a continuous accumulation of this compound in the vulcanizing compound (Figure 14).

The benzothiazolyl and diethylamine radicals, formed during the initial thermal dissociation of Sulfenamide BT, as with the polymer radical, arising as a result of the extraction of hydrogen from the molecular chains of the rubber, evidently are free to interact independently with the sulfur, breaking the eight membered rings of the sulfur thereby guaranteeing the interaction of the sulfur with the rubber.   Together with this process there occurs the interaction of the polymer radicals with themselves and with the molecules of rubber with the formation of carbon-carbon bonds into a vulcanized structure.   The presence of these bonds is observed in the behavior of vulcanizates during their chemical relaxation[11].
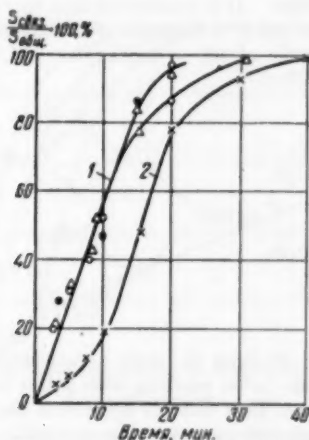
Fig. 15.—The influence of various derivatives of MBT on the kinetics of the addition of sulfur.   1—MBT, MBTS; 2—Sulfenamide BT.

The cause of the particular type of kinetics and the presence of the induction period during vulcanization in the presence of Sulfenamide BT.—The particular type of rate curve with an induction period and the presence of self acceleration is characteristic of investigations of Semenov and his school of chain reactions with degenerative branching[12].   However, the reaction mechanism with degenerative branching cannot be carried over to the case in question since we have no data confirming the formation of stable intermediary compounds, the decomposition of which would make possible the formation of additional reaction chains.   Thus it is necessary for us to set forth a special explanation for the phenomenon.

The presence of an initial period of inhibited sulfur addition (the part which we call the induction period) is a property characteristic for sulfenamide produced MBT.   As may be seen in Figure 15, this period is not observed in the rate curves for vulcanizates from mixes with the accelerators MBT and MBTS. The length of the induction period depends on the character of groups attached to the nitrogen of the sulfenamide group[13].   The hypothesis about the inhibiting action of oxygen as the cause of the induction period has not been substantiated by the experimental data shown above.   The action of other additional "impurities" was also excluded since the induction period is lengthened rather than shortened in purified rubber.   Thus it is necessary to conclude that

the particular nature of the kinetics of the addition of sulfur in the presence of sulfenamides is connected with the way this accelerator acts.

As was shown above, the rate and energy of activation (30 kcal per mole) for the addition of sulfur in the initial period was essentially the same as that observed for the addition of sulfur in the absence of accelerator. From this it is possible to conclude that the molecular form of N,N-diethyl-2-benzothiazolyl-sulfenamide does not activate the sulfur. The activating action appears with the formation of benzothiazolyl and diethylamine radicals which are formed by the thermal dissociation of sulfenamide (scheme 1) and, in particular, with the formation of MBT and diethylamine arising as a result of the reaction of the sulfenamide with the rubber. If it is assumed that this reaction goes according to scheme 3, every interaction of a molecule of sulfenamide with rubber leads to the formation of a molecule of active accelerator and two radicals which are able to react with the sulfur:
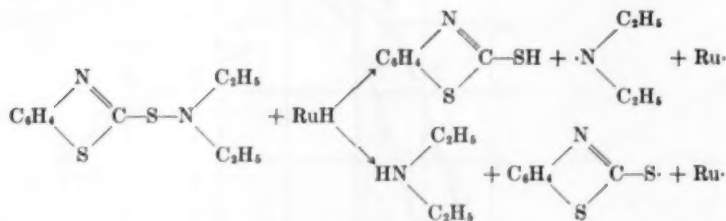
In other words, each reacting molecule of accelerator is replaced by three groups which are active so far as reacting with sulfur is concerned. A similar development of the process must sharply accelerate the addition of sulfur: the transition from the initial period to the main period.

The activation energy of the addition of sulfur during the main period is equal to 14 kcal per mole which is substantially greater than the value accepted for a chain radical process. As has been shown in the work of Dogadkin and others, each time an accelerator radical is formed during the vulcanization of rubber there are from 0.6 to 2.7 elementary instances of molecular chains combining. To wit, the limited growth of the reaction chain, being determined by the nature of the thermal motion of the rubber molecule, may serve as one of the causes of the increase in activation energy of the reaction in question.

The increased rate of the addition of sulfur to rubber in the main period is connected with the following peculiarities of the process. As is seen in the experimental data, during the progress of the process, a significant number of the N,N-diethyl-2-benzothiazolylsulfenamide molecules are transformed to twice that number of molecules of two new accelerators: MBT and diethylamine.

From Figure 16 it can be seen that the action of these two accelerators is not additive: a mixture of them accelerates the addition of sulfur to rubber to a greater degree than does each accelerator when taken separately at the same molecular concentration. The cause of the increased activity of the mixture of the two accelerators consists, evidently, of the formation of an intermediate compound which facilitates the emergence of free radicals of the vulcanization agent[15].

The particular type of kinetics of the addition of sulfur to compounds with Sulfenamide BT is, naturally, reflected in the dynamics of the formation of crosslinks and changes in the plastoelastic properties of the compound. In the

absence of other accelerators (TMTD, MBT and others) the Sulfenamide BT guarantees that the compound will remain in a viscous state for a certain length of time (the induction period) during which there are several phases where the plasticity of the compound being vulcanized increases in spite of the addition of sulfur.   This shows that Sulfenamide BT is able to cause thermal and oxidative rupturing of the molecular chains of the rubber.   There is basis for the belief that the rupture of the molecules of rubber under the action of N,N-diethyl-2-benzothiazolylsulfenamide occurs by the same mechanism that was established for free radicals by Pike and Watson[14].
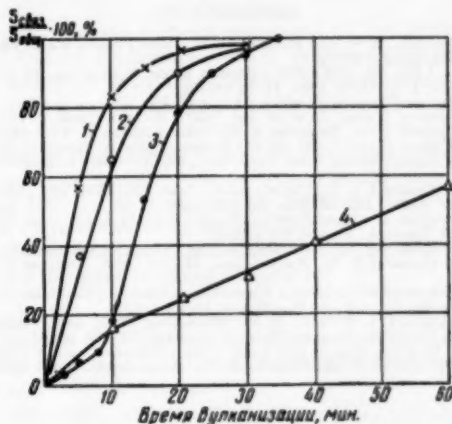
FIG. 16.—The kinetics of the addition of sulfur in the presence of accelerators.   1—MBT +diethylamine; 2—MBT ; 3—Sulfenamide BT ; 4—diethylamine.

CONCLUSIONS

1. The vulcanization of rubber in the presence of N,N-diethyl-2-benzo-thiazolylsulfenamide is characterized by an S-shaped curve for the addition of sulfur with an initial induction period in the reaction.   The modulus and number of crosslinks are changed in an analogous manner to the structure of the vulcanizate.

2. The energy of activation of the addition of sulfur in the initial period is equal to 30 kcal per mole as against 14 kcal per mole in the main period.

3. The induction period is increased if the sodium-butadiene rubber is purified from alkali.

4. Molecular oxygen present in the compound being vulcanized decreases the induction period and increases the rate of the addition of the sulfur in the main period.   An induction period is not observed when vulcanization is carried out in an atmosphere of pure oxygen.

5. The interaction of N,N-diethyl-2-benzothiazolylsulfenamide with rubber (in the absence of sulfur) at vulcanization temperatures is accompanied by the formation of MBT, diethylamine, and the addition of the elements of the accelerator to the rubber.   The kinetics of this process were studied.

6. The interaction of N,N-diethyl-2-benzothiazolyl sulfenamide with rubber leads to the formation of chemical crosslinks between the molecules of rubber (the effect of vulcanization).

7. The change of N,N-diethyl-2-benzothiazolyl sulfenamide under the conditions of normal sulfur vulcanization has the same character as in the interaction of it with rubber.   The kinetics of the formation of MBT have a maximum which coincides with the maximum rate of the addition of sulfur to the rubber.

8. A mechanism is presented for the vulcanization and acceleration actions of N,N-diethyl-2-benzothiazolyl sulfenamide which provides for the extraction of hydrogen by the accelerator radicals from the molecular chains of the rubber with the formation of MBT, diethylamine and polymer radicals which are able to interact with the sulfur.

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THE ACTION OF BINARY ACCELERATOR SYSTEMS OF VULCANIZATION *

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The use of vulcanization systems composed of two or more accelerators finds wide technological application. Such systems generally possess an increased activity over that obtained with the individual components. In spite of the wide practice of using combinations the mechanism of the joint action of the accelerators has been inadequately studied and the principles of compounding with binary and ternary accelerator systems have not been established. The increase in activity arising from the use of two accelerators is considered to be the result of formation between them[1, 2, 3] of a salt-like complex which is more active than either alone.

This paper presents the results of a study of a number of binary systems of accelerators having different chemical structures:

(a) Organic disulfides and nitrogen containing organic bases: benzothiazolyl disulfide (MBTS)—diphenylguanidine (DPG), MBTS—hexamethylenetetramine (Hexa), dimethylthiocarbamoyl disulfide (TMTD) —DPG, and TMTD—Hexa.

(b) Organic disulfides and sulfenamides: MBTS—N,N-diethyl-2-benzothiazolylsulfenamide (DEBTS), MBTS—N-cyclohexyl-2-benzothiazolylsulfenamide (CHBTS), and TMTD—CHBTS.

(c) Sulfenamides and nitrogen containing organic bases: CHBTS—DPG, DEBTS—DPG, CHBTS—Hexa, DEBTS—Hexa.

(d) Mercaptans and nitrogen containing organic bases: mercaptobenzothiazole (MBT) with DPG, Hexa or melamine.

(e) Sulfenamides (CHBTS, DEBTS) and disulfides (MBTS), with dimethylthiocarbamoyl monosulfide (TMTM).

As can be seen from this list, the study was made with the most popular accelerators.

The dynamics of vulcanization of styrene-butadiene rubber (SBR) in the presence of the above mentioned accelerator combinations were studied in compounds of the following compositions: rubber (SKS-30 AM), 100 parts; stearic acid, 2 parts; accelerators, in varying quantities; zinc oxide, 5 parts; channel black, 30 parts; sulfur, 2 parts. In all cases thermoplasticated SKS-30 AM with a Karrer plasticity of 0.5–0.55 was used.

The dynamics of vulcanization of the compounds were studied by means of the physical properties, data on sulfur combined with the rubber, and degree of swell.

In addition, experiments were made to determine the nature of the reaction of some accelerators with each other in solvent medium and in the presence of rubber.

DYNAMICS OF VULCANIZATION OF RUBBER COMPOUNDS

Disulfides and nitrogen containing organic bases.—In the case of the systems, MBTS-DPG, MBTS-Hexa and TMTD-Hexa there was observed a mutual action of the accelerators.

In Figure 1 there is shown the change of physical properties of compounds containing MBTS-DPG. From the data given on the abscissa it follows that with the different combinations of accelerators the sum of the molecular con-
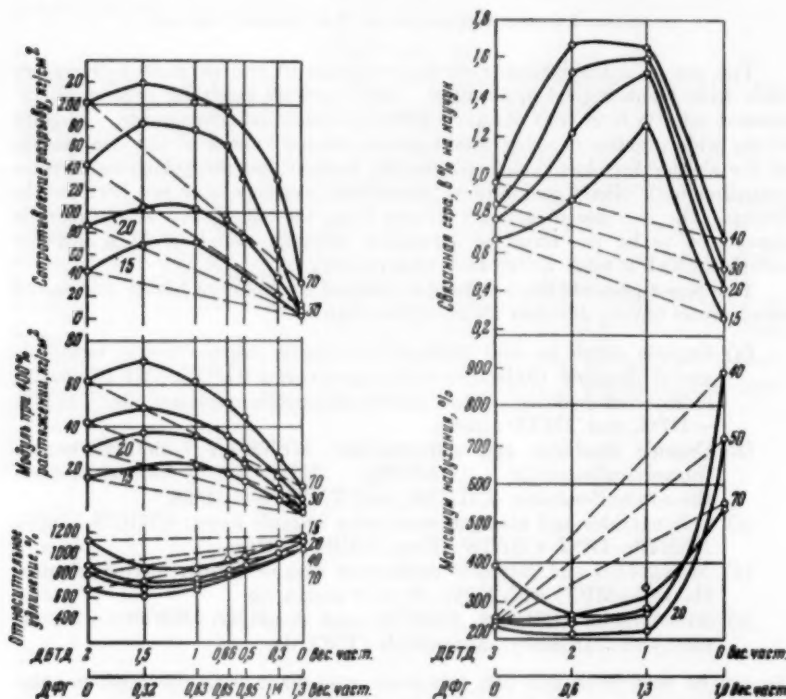
Fig. 1.—The action of the binary system, MBTS-DPG. Upper abscissa; MBTS, weight parts. Lower abscissa; DPG, weight parts. Ordinates, from top to bottom: Tensile strength, kg/cm²; Modulus at 400% elongation, kg/cm²; Relative elongation, %.

Fig. 2.—Combined sulfur content and maximum swell of compounds vulcanized with MBTS-DPG mixtures. Abscissa; same as for Figure 1. Ordinates, from top to bottom: Combined sulfur, % on the rubber; Maximum swell, %.

centrations remains constant. The straight broken lines on this and the following figures which connect the indexes of vulcanization activity of the single accelerators indicate the change of properties corresponding to additive action of the accelerators.

The data in Figure 1 (the numbers on the curves represent vulcanization time in minutes) show that in this case the action of the accelerators is not additive. Any ratio of MBTS to DPG provides a higher strength and modulus, a larger quantity of combined sulfur and lower value of maximum swell (Figure 2) in the rubber compounds than does each accelerator separately.

Similar action is characteristic of the other accelerator systems with these structures.

Disulfides and sulfenamides.—All three systems studied—MBTS-DEBTS, MBTS-CHBTS, and TMTD-CHBTS—display considerable mutual activation, resulting in an increase in strength and modulus of rubber compound in comparison with vulcanizates of compounds containing these accelerators separately. The system MBTS-CHBTS behaves the same as the system MBTS-DEBTS (Figure 3). In these cases the maximum activation of accelerator is observed at ratios near equimolar. It is interesting to note that in the system which contains 0.33 part MBTS and 1.2 parts DEBTS slower vulcanization was noticed—decrease in strength and modulus.
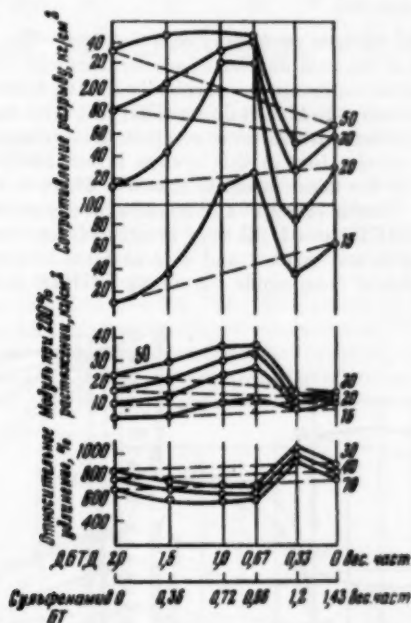
Fig. 3.—The action of the binary system, MBTS-DEBTS. Upper abscissa; MBTS, weight parts. Lower abscissa: DEBTS, weight parts. Ordinates from top to bottom: Tensile strength, kg/cm²; Modulus at 200% elongation, kg/cm²; Relative elongation, %.

Data obtained on kinetics of vulcanization of rubber compounds containing MBTS and DEBTS confirm the previously noted fact for the system TMTD-MBTS[4], that the vulcanization is slow in the early stages. As is seen from the data on addition of sulfur in the early stages of the vulcanization process on channel black compounds of SBR (Figure 4, curve for 5 minutes), the two accelerator system causes less effect on the vulcanization than each accelerator separately. In the later stages of vulcanization (after 10 min) there occurs an increase in the vulcanization activity as shown by the data on changes of physical properties of the vulcanizates (Figure 3). The delay of vulcanization in the first 5–10 minutes is also quite noticeable in the vulcanization of unfilled compounds.
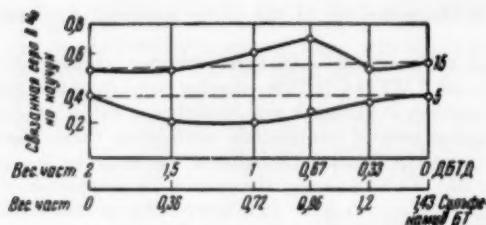
Fig. 4.—Change in combined sulfur content of vulcanizates containing MBTS-DEBTS. Upper abscissa: MBTS, weight parts. Lower abscissa; DEBTS, weight parts. Ordinate; Combined sulfur, % on the rubber.

Sulfenamides and nitrogen containing organic bases.—The data of Figure 6 illustrate the action of the combination of accelerators with these groups on the vulcanization of rubber compounds, specifically for the system CHBTS-DPG. The use of DPG in compounds containing CHBTS lowers the tensile strength and the modulus in comparison with compounds containing only CHBTS. The action of the accelerators in this system is not additive. In this case mutual activation of the accelerators is absent. There is only activation of DPG by CHBTS. Tensile strength and modulus of compounds which contain a combination of CHBTS and DPG very greatly surpass the values obtained with DPG alone but do not surpass, and in some cases do not reach, the tensile strength and modulus of compounds containing CHBTS alone. The data on
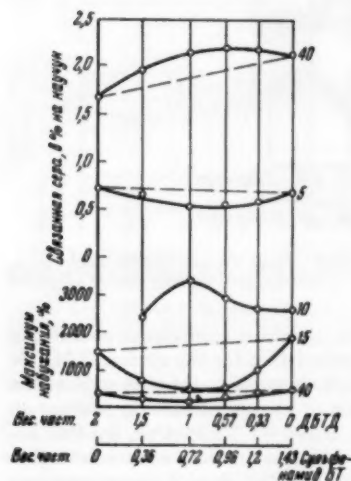
Fig. 5.—Change of combined sulfur and maximum swell of unfilled compounds containing MBTS-DEBTS. Upper abscissa; MBTS, weight parts. Lower abscissa; DEBTS, weight parts. Ordinates, top to bottom: Combined sulfur, % on the rubber; Maximum swell, %.
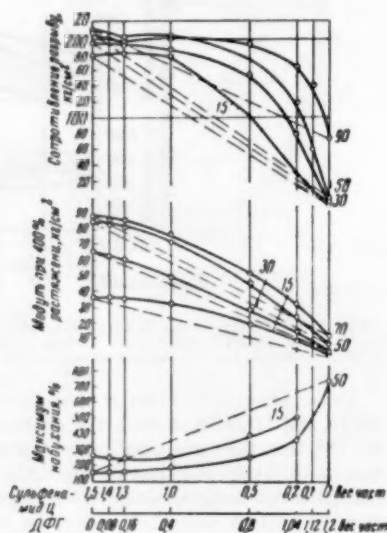
Fig. 6.—Action of the binary system, CHBTS-DPG. Upper abscissa; CHBTS, weight parts. Lower abscissa; DPG, weight parts. Ordinates, from top to bottom: Tensile strength, kg/cm²; Modulus at 400% elongation, kg/cm²; Maximum swell, %.
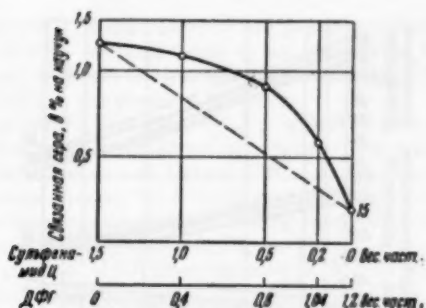
Fig. 7.—Change of combined sulfur content of vulcanizates containing DEBTS-DPG. Upper abscissa; DEBTS, weight parts. Lower abscissa; DPG, weight parts. Ordinate; combined sulfur, % on the rubber.

kinetics of addition of sulfur (Figure 7) verify the conclusion that for the systems mentioned activation of only one accelerator takes place—the nitrogen containing organic base.

Mercaptans and nitrogen containing organic bases.—Such a combination of accelerators is similar to the disulfide-organic base systems. In particular, the action of the system MBT-DPG (Figure 8) on vulcanization is analogous to that of the system MBTS-DPG (see Figure 1). There is clearly observed a mutual activation of accelerators.

Sulfenamides or disulfides and TMTM.—The action of TMTM when used together with the calculated optimum concentration of DEBTS, CHBTS or MBTS was studied. Such a combination of accelerators, as can be seen from Figure 9 representing the kinetics of vulcanization of rubber compounds in the presence of CHBTS-TMTM, has an approximately additive effect on vulcaniza-
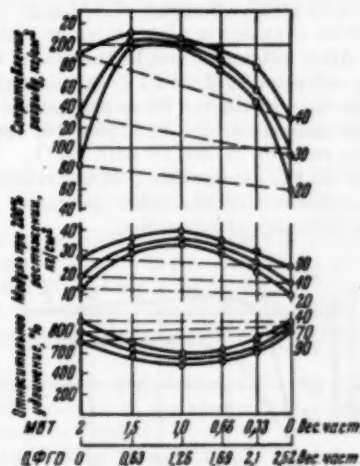
Fig. 8.—Action of the binary system MBT-DPG. Upper abscissa; MBT, weight parts. Lower abscissa; DPG, weight parts. Ordinates, from top to bottom: Tensile strength, kg/cm²; Modulus at 200% elongation, kg/cm²; Relative elongation, %.
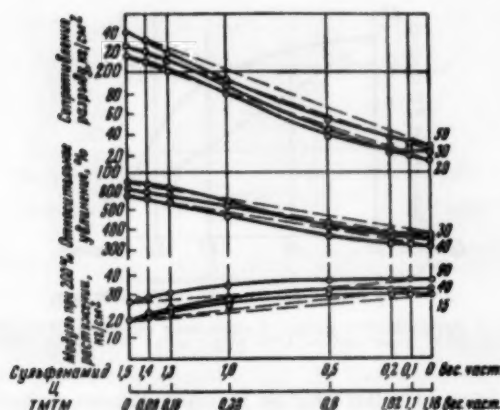
Fig. 9.—Action of the binary system CHBTS-TMTM. Upper abscissa; CHBTS, weight parts. Lower abscissa; TMTM; weight parts. Ordinates, from top to bottom: Tensile strength, kg/cm²; Relative elongation, %; Modulus at 200% elongation, kg/cm².

tion kinetics.   The values of strength, modulus and relative elongation of rubber compounds vulcanized with this system lie on curves close to the broken straight lines representing additive action of the accelerators.   Analogous action occurs with binary systems of accelerators belonging to one class of chemical composition, such as the combination CHBTS-DEBTS.

REACTION OF VULCANIZATION ACCELERATORS
IN A SOLVENT MEDIUM

Reaction of MBTS with DPG.—Samples of 0.71 g CP MBTS and 0.45 g CP DPG were sealed in 30 ml of xylene in glass ampoules and placed in a thermostated bath at 140°.   After different times the ampoules were opened and the reaction mixtures were extracted cold with 1% caustic soda in order to extract MBT as a possible reaction product.   From the caustic solution MBT was precipitated with dilute sulfuric acid.   In Figure 10, curve *I* represents the yield of MBT from the reaction of MBTS with DPG.   The yield is 3.16 g/l which is 30% of theory on the assumption that the reaction takes place in an equimolar ratio.   Identification of the other products of reaction was not possible because of the difficulty of separation.
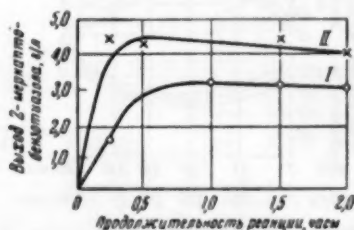
Fig. 10.—Yield of MBT by reaction of MBTS with DPG in xylene at 140° in the presence of sulfer (*II*) and without sulfur (*I*) Abscissa; Time of reaction, hours.   Ordinate; Yield of MBT, g/l.

The reaction of MBTS with DPG in the presence of 0.55 g of sulfur (equimolar with the MBTS content) leads to an increase in the yield of MBT. Curve *II* of Figure 10 shows the kinetics of formation of MBT by the reaction of MBTS with DPG in the presence of sulfur.

The reaction of MBTS with Hexa.—0.7 g cp MBTS and 0.3 g cp Hexa were placed in glass ampoules with 30 ml of xylene. The sealed ampoules were heated for different times at 140, 160 and 170°. In the experiments at 160° and 170°, the xylene was replaced by a fraction of white spirits (a turpentine substitute) free from unsaturation, with a boiling range of 150°–180°. The yield of MBT from the reaction is shown in Figure 11.

At 140° the yield of MBT from reaction of MBTS with Hexa decreases sharply in comparison to the reaction of MBTS with DPG. Higher temperatures give an increased yield of MBT.
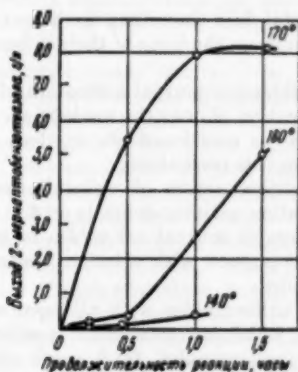
FIG. 11.—Yield of MBT by reaction of MBTS with Hexa at 140°, 160° and 170°. Abscissa: time of reaction, hours. Ordinate: Yield of MBT, g/l.

Reaction of CHBTS with MBTS.—Samples of 1.0 g cp CHBTS with 1.2 g cp MBTS in one case, and 1.0 g cp CHBTS with 0.8 g cp MBTS in another case were sealed in ampoules with 30 ml of xylene or white spirits. The compounds were heated at 150°, 160° and 170°. No production of MBT was observed.

REACTION OF VULCANIZATION ACCELERATORS IN THE PRESENCE OF RUBBER

The experiments on reaction of accelerators in the presence of rubber were also carried out in sealed ampoules as described in the preceding section with the difference that the solvent was replaced with a 2.5% solution of sodium butadiene rubber [SKB-Pishchevoi (digestible)] in xylene. The purification of the SKB from residual alkali was done by the method worked out by Dobromyslova[5].

At the end of the reaction period the MBT was separated. The yield of MBT as a result of the reaction of the accelerators in rubber solution is given for a number of systems in Table I.

Figure 12 gives data on the yield of MBT from the reaction of MBTS with CHBTS (in different ratios), obtained by heating the rubber solution. In this case there is observed a considerably greater yield of MBT than would be expected if the action of the accelerators was independent (broken line, Figure 12).
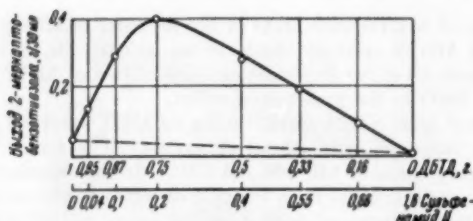
Fig. 12.—Yield of MBT by reaction of MBTS with CHBTS on heating in rubber solution. Time of reaction, 90 minutes; temperature, 150°. Upper abscissa; MBTS, g. Lower abscissa; CHBTS. Ordinate; Yield of MBT, g/30 ml.

DISCUSSION OF RESULTS

The above experimental data show that the binary accelerator systems can be divided into three groups on the basis of their influence on the vulcanization process.

1. Systems with considerable mutual activation of the accelerators.

2. Systems with activation of one (the weaker) accelerator. Vulcanization activity of such systems, as mentioned above, does not surpass that of the stronger accelerator when it is used alone.

3. Systems with additive action of vulcanization accelerators. Within one system the vulcanization activity depends on the ratio of the accelerators.

Systems with considerable mutual activation of accelerators include mixtures of disulfides or mercaptans with nitrogen containing organic bases and disulfides with sulfenamides.

The combination of sulfenamides with nitrogen containing organic bases belongs to the system in which one accelerator is activated.

Systems containing sulfenamides (and some disulfides) together with TMTM, and those containing combinations of accelerators belonging to the same chemical class, are characterized by an additive action of the accelerators.

TABLE I

YIELD OF MBT BY THE REACTION OF ACCELERATORS IN SOLVENTS AND IN RUBBER SOLUTION

(TIME OF REACTION—1.5 HOURS)

No. of system	Reacting substances	Characteristic chemical bond of reacting substances	Sample size of reacting substances, g/30 ml of solution	Yield of MBT			
				In xylene at 150°	In white spirits		In 2.5% solution SKB rubber at 150°
					160°	170°	
1	MBTS	—S—S—	1.0 + 1.26	—	—	—	0.83
2	CHBTS	—S—N—	0.5 + 0.63	Trace	—	—	0.40
	CHBTS	—S—N—	1.0 + 0.8	—	—	—	0.25
3	DPG	—N—H	0.71 + 0.57	Trace	None	None	0.17
	CHBTS	—S—N—	1.0	None	None	None	0.025
4	MBTS	—S—S—	1.26	—	—	—	0.15
			0.63	None	None	—	0.08

The formation of MBT by reaction between accelerators in solvent medium (reaction of MBTS with DPG) and also in the presence of rubber (CHBTS with MBTS and with DPG) indicates that in the cases studied reaction took place between the accelerators.

Therefore, the data obtained by us do not show agreement with the points of view expressed by a number of scientists[1, 2, 3] that the activation of accelerators when used together is due to the formation of salt-like molecular compounds which possess higher vulcanization activity. The theories set forth below concerning the mechanism of mutual action of accelerators are a further development resulting from our presentation on free radical action of vulcanization accelerators[6, 7, 8].

There is reason to think that in the use of joint accelerators, three radicals are formed as a result of reaction between them. The formation of the free radical can occur as a result of thermal decomposition of the accelerators under the vulcanization conditions or as a result of chemical reaction between them. The latter probably occurs with less energy than the thermal dissociation and thus provides a larger concentration of free radicals.

It is known that the chemical behavior of organic disulfides is analogous in a number of cases to the action of organic peroxides. Like peroxides, disulfides easily oxidize hydrogen iodide to free iodine, and both are subject to thermal and photochemical decomposition to free radicals. Thanks to this, disulfides as well as peroxides can behave as initiators of polymerization[6, 11]. If organic peroxides can dissociate into radicals[9, 10] under the influence of amines, then it can be assumed that organic disulfides can also dissociate into free radicals under the influence of amines. There is no direct literature information on the existence of such a reaction, but in the work of Guryanova[12] there is noted the role of dibutylamine as a catalyst of the exchange reaction between organic disulfides and polysulfides, a reaction with free radical mechanism.

We assume that under vulcanization conditions the reaction of disulfides with nitrogen containing organic bases (specifically MBTS with DPG) occurs in the following manner.

1. $RSSR + R'R''NH \longrightarrow \begin{bmatrix} RSSR \\ R'R''NH \end{bmatrix} \longrightarrow RSH + RS\cdot + R'R''N\cdot$

Chain initiation

2. $RS\cdot + R'R''NH \longrightarrow RSH + R'R''N\cdot$

3. $R'R''N\cdot + RSSR \longrightarrow RSNR''R' + RS\cdot$

4. $RSSR + RSNR'R'' \longrightarrow \begin{bmatrix} RSSR \\ RSNR'R'' \end{bmatrix} \longrightarrow 3RS\cdot + R''R'N\cdot$

Chain propagation

5. $RS\cdot + R''R'N\cdot \longrightarrow RSNR'R''$

6. $RS\cdot + RS\cdot \longrightarrow RSSR$

Chain termination

7. $R'R''N\cdot + R'R''N\cdot \longrightarrow R'R''NNR''R$

where R = ... R' = ... and R'' = ...
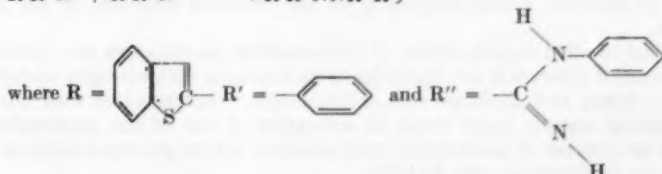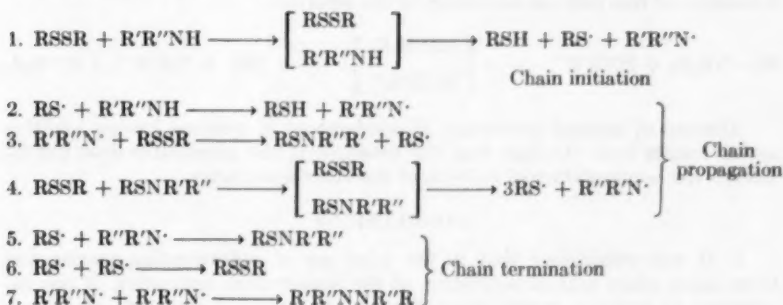
The radicals formed by reaction between accelerators can initiate other free radical processes, in particular the crosslinking of rubber molecules in the vulcanization process.

The identification of MBT as one of the products of the reaction of MBTS with DPG at 140° in xylene confirms the assumed scheme to some degree. The identification of the other reaction products (based on the assumed reaction), benzothiazolylsulfendiphenylguanidine (RSNR′R″) and bis-diphenylguanidine (R′R″NNR″R′) was not successful because of the difficulty of separating them from the mixture.

It is necessary to point out that the given reaction scheme includes, in steps 3 and 5, the formation of sulfenamide compounds of the type widely used as vulcanization accelerators. According to the scheme the sulfenamides themselves can cause radical decomposition of disulfides (Step 4). This is confirmed by the data on the study of the chemical reaction of MBTS with CHBTS, specifically by the absence of formation of MBT by reaction in pure solvent and the intensity of the reaction in the presence of rubber which acts as a hydrogen donor (Table I and Figure 12). The formation of a considerably larger quantity of MBT in comparison with what would be observed if the actions of the reacting accelerators in this system were independent of each other, establishes that the principal result of the chemical reaction of the accelerators is the appearance of a considerable quantity of free radicals which split out hydrogen from the molecular links of rubber with the formation of rubber high polymer radicals. This explains the mutual activation of accelerators in systems of disulfides with nitrogen containing organic bases and with sulfenamides.

The activation of accelerators in the system of mercaptans and nitrogen containing organic bases also appears to be due to the existence of the radical reaction between the accelerators.

This assumption is also true for the systems of sulfenamides and nitrogen containing organic bases. It is known that amines are capable of mutual displacement of each other from their derivatives[12]. On this basis we think that sulfenamides and amines can react with each other with the intermediate formation of free radicals according to the equation:

$$RS{-}NR_1R_2 + HNR′R″ \longrightarrow \begin{bmatrix} RSNR_1R_2 \\ HNR′R″ \end{bmatrix} \longrightarrow [RS{\cdot} + {\cdot}NR′R″] + HNR_1R_2$$
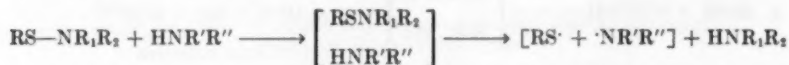
Absence of mutual activation of accelerators in systems having additive action results from the fact that the presence of one accelerator does not influence the accumulation of radicals of the other accelerator.

CONCLUSIONS

1. It was established that in the joint use of vulcanization accelerators there takes place mutual activation of the accelerators, activation of one accelerator or additive action depending on the chemical structure of the accelerators.

2. Of the studied combinations of vulcanization accelerators the systems showing mutual activation are disulfides or mercaptans with nitrogen containing organic bases, and disulfides with sulfenamides. Sulfenamides with nitrogen containing organic bases result in activation of one of the accelerators. Examples of systems of accelerators with additive action are combinations of sulfenamides or disulfides with TMTM.

3. It was established that in the case of systems with mutual activation, such as MBTS with DPG or with CHBTS, the reaction between the accelerators produces MBT. For such systems, greater yields of MBT were observed under vulcanization conditions than were obtained by action of the accelerators alone. This indicates that the principal result of the chemical reaction of the accelerators is the formation of free radicals which are capable of splitting hydrogen from the rubber molecule with the formation of rubber high polymer radicals.

4. There is presented a tentative scheme for a radical mechanism of the joint action of vulcanization accelerators for the case where mutual activation of accelerators exists.

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COMPOSITION OF VULCANIZING SYSTEM, COURSE OF VULCANIZATION AND BOND STRENGTH OF PLIED–UP SBR *

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Insufficient bond strength between individual plies, in particular between the breaker strip and tire tread, is one of the shortcomings of tires manufactured from SBR rubbers. For several reasons, one of which is the conditions in which such large articles as tires are vulcanized, the breaker strip contains a much more active vulcanizing system than the tread rubber. The vulcanization of these rubbers in a zone of direct contact is effected at virtually the same temperature. In considering the special features of the vulcanization of SBR rubber, as one which vulcanizes comparatively slowly, it was natural to expect that the different activities of the vulcanizing systems in joined plies condition a sharp difference in the course of vulcanization, which might affect the bond strength considerably.

We therefore made a study of the effect of the composition of crosslinking system and kinetics of vulcanization on the bond strength of plied-up SKS 30 rubber.

The composition of the crosslinking system was determined mainly by the type of accelerators used and their loading. The following were used as accelerators; a combination of MBTS and DPG, Sulfenamide BT, Santocure, TMTD and a combination of TMTD and MBTS. Part of the experiments was conducted on specimens with plied-up layers differing only in the composition of the vulcanizing system. Construction was effected as follows: breaker strip—breaker strip or tread—tread. In addition, three-layer systems were also studied: tread—breaker strip—tread. In all cases construction was effected: (a) without using an adhesive layer and (b) using an adhesive of SKS-30A.

In some experiments a two-rubber adhesive was also used, consisting of 75% SKS-30A and 25% natural rubber. The same crosslinking system was introduced into the adhesive as into the breaker strip stock.

The following three methods were used to evaluate the bond strength of two-ply layers vulcanized at a temperature of 133° or 143°:

(a) measuring the specific energy of ply separation;

(b) determining the specific resistance to ply separation of diagonal two-ply specimens with repeated compression; and

(c) determining the resistance to dynamic ply separation with the repeated shear of two-layer specimens, with the plane of the joint in a normal position to the direction of shear.
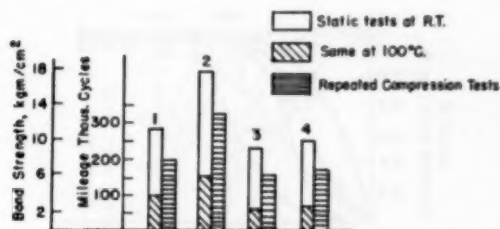
FIG. 1.—The effect of the composition of the vulcanizing system on the bond strength of two-layer rubbers:

Composition of the vulcanizing system in phr:

	1	2	3	4
Sulfur	3.0	2.0	2.0	2.0
MBTS	0.8	—	—	1.5
DPG	0.8	—	—	—
Sulfenamide BT	—	1.2	—	—
TMTD	—	—	0.4	0.25

The bond strength of rubbers containing similar vulcanizing systems in both layers is shown in Figure 1. From the diagram it can be seen, depending on the accelerators which enter into the composition of the vulcanizing system (if this composition guarantees similar physical properties at optimum cure), that systems containing Sulfenamide BT will have the greatest bond strength. Hence plied-up rubbers containing Sulfenamide BT in both layers showed considerably higher bond strength in static and dynamic tests than systems which contained combinations of other accelerators: MBTS—DPG, MBTS—TMTD or TMTD alone. In particular, replacing MBTS-DPG with Sulfenamide BT increased the dynamic resistance to ply separation in repeated compression tests from 185,000 to 32,000 cycles.

TABLE 1

RESISTANCE TO PLY SEPARATION OF THE SYSTEM TIRE TREAD— BREAKER STRIP—TIRE TREAD

Composition of vulcanizing system in phr		Plying-up effected	Cure time, min at 143°	Data on the dynamic testing of specimens with repeated shear			
				Life, cycles	Form of failure, %		
Breaker Strip	Tread				Ply separation	Ply separation with failure of the breaker strip	Failure
Sulfur—3.0	Sulfur—2.0	Without an adhesive	70	256	80	20	—
MBTS—0.8	MBTS—0.5	With an adhesive (SKS-30 and natural rubber)					
DPG—0.8	DPG—1.0			175	100	—	—
Sulfur—3.0	Sulfur—1.5	Without an adhesive	100	288	60	40	—
MBTS—0.6	MBTS—1.0						
DPG—0.6	DPG—0.5	With an adhesive		187	100	—	—
Sulfur—3.0	Sulfur—1.5	Without an adhesive	130	852	—	40	60
MBTS—0.4	MBTS—0.8						
DPG—0.4	DPG—0.4	With an adhesive		338	60	40	—
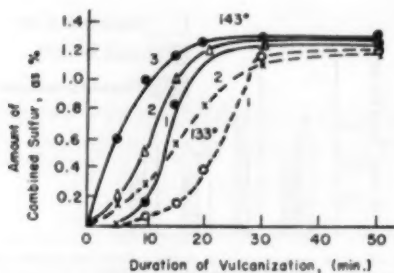
FIG. 2.—Rate of crosslinking with sulfur in unfilled stocks at vulcanization temperatures of 133° and 143°. Accelerator concentration, phr: curve 1, Sulfenamide BT—1.0 part by weight; 2, Santocure—1.0 part by weight; 3, MBTS—0.5 part by weight, DPG—1.0.

One of the main objects of the present study was to explain the positive effect on the bond strength of plied-up butadiene-styrene rubbers produced by Sulfenamide BT compared with other accelerators.

The series of experiments showed that the bond strength of multiply butadiene-styrene rubbers can be increased considerably by retarding the vulcanization process in its initial stages. This control was effected by reducing the concentration of accelerators. The length of the process was such as to guarantee practically the same degree of vulcanization as determined by modulus.

From the data in Table I (see also Figure 3), it can be seen that the slowing up of vulcanization in the first stage of the process, with the required physical properties being reached at a later stage, reflects favorably on the bond strength of the specimens.

We were interested in finding out whether the positive effect of the Sulfenamide BT on the monolithic nature of the structure of multiply articles was connected with certain features of the kinetics of the vulcanization of rubber stocks in the presence of this accelerator.

A comparative study of the kinetics of vulcanization of SBR in the presence of various accelerators was carried out on unfilled and filled stocks. The former were selected to avoid the specific effect that active fillers have on the course of vulcanization. Hence when compared with combinations of MBTS and DPG, sulfenamide accelerators retard the cure rate in the initial stage of the process. This results in the reactions of structurization being slowed up, and this is shown by the data on the variation of the equilibrium modulus given in Figure 3. The equilibrium modulus of the stock containing Sulfenamide BT, after
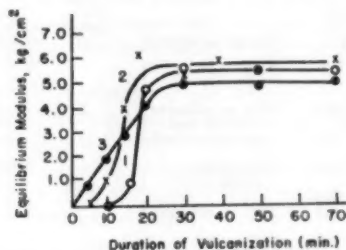
FIG. 3.—The variation in equilibrium modulus as a function of the duration of vulcanization. Curve 1, Sulfenamide BT; 2, Santocure; 3, MBTS and DPG.
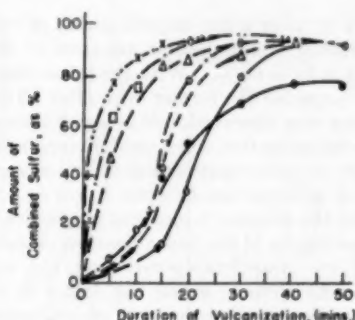
FIG. 4.—Rate of sulfur combination depending on both type and content of accelerator.

Sulfenamide BT	MBTS + DPG
1. 0.8 part by weight	*4*. 0.4 part by weight +0.4 part by weight
2. 1.0 part by weight	*5*. 0.6 part by weight +0.6 part by weight
3. 1.2 parts by weight	*6*. 0.6 part by weight +0.75 part by weight
	7. 0.8 part by weight +0.8 part by weight

five and even ten minutes of vulcanization, is zero which shows that in the presence of Sulfenamide BT the formation of a network has still not occurred after the first ten minutes of vulcanization.

The induction period of vulcanization conditioned by the sulfenamide accelerators is not a particular feature of the corresponding ratio between the sulfur and accelerator, but it does in fact depend on the nature of the latter.

Figure 4 shows rate curves for the combination of sulfur using varying amounts of Sulfenamide BT and their equimolecular amounts of MBTS and DPG. The amount of reacted sulfur in stocks containing 1.0 and 1.2 parts by

TABLE 2

VARIATION IN THE MAXIMUM SWELLING OF UNFILLED STOCKS DEPENDING ON THE CONCENTRATION AND TYPE OF ACCELERATOR

Composition of the vulcanizing system, phr	Cure time, min.					
	5	10	15	20	30	40
			Swell, %			
Sulfur—2.0 Sulfenamide BT—0.8	Unlimited swelling		Gel	667	465	385
Sulfur—2.0 Sulfenamide BT—1.0	Unlimited swelling	Gel	1600	485	425	—
Sulfur—2.0 Sulfenamide BT—1.2	Gel		450	387	390	—
Sulfur—2.0 Sulfenamide—1.5	Gel	780	357	348	360	—
Sulfur—2.0 MBTS—0.4 DPG—0.4	Unlimited swelling		1800	1190	900	—
Sulfur—2.0 MBTS—0.6 DPG—0.6	Unlimited swelling	1100	535	525	500	—
Sulfur—2.0 MBTS—0.6 DPG—0.75	607	499	450	475	445	—
Sulfur—2.0 MBTS—0.8 DPG—0.8	445	415	470	420	408	—

weight Sulfenamide BT is, after a five minute period of vulcanization, 6 to 9%
while for the corresponding equimolecular amounts of MBTS and DPG the
amount of linked sulfur is 50 to 65%. With the latter limited swelling was also
observed (Table 2), whereas for the former even after 10 minutes vulcanization
only slight gel formation was observed. Whereas Sulfenamide BT conditions
an induction period of vulcanization when used in varying amounts with sulfur,
MBTS and DPG show an induction period of vulcanization with only very
small concentrations of accelerators (Figure 4, curve 4), and these are not
capable of guaranteeing the necessary physical properties. Hence when using
MBTS and DPG a slowing up of the vulcanization process in its initial stages
can only be effected by considerably reducing the concentration of the
vulcanization system. As already noted the latter is so weak as to be of
no technical interest. One special feature of sulfenamide accelerators is
that they retard vulcanization in its initial stages, bringing about increased
intensity of vulcanization at a subsequent stage. Without increasing the over-
all duration of the period of vulcanization, this process allows us to obtain
vulcanizates with the necessary technical properties.

TABLE 3

VARIATION IN THE INITIAL VULCANIZATION TEMPERATURE AT 40 MINUTES
FOR VARIOUS VULCANIZING SYSTEMS (UNFILLED STOCKS OF SKS-30A)

Composition of vul-canizing system, phr	Cure temperature, ° C				
	105	110	115	120	130
		Swell, %			
Sulfur—3.0 MBTS—0.8 DPG—0.8	unlimited swelling	1634	899	502	401
Sulfur—3.0 MBTS—0.5 DPG—0.5	unlimited swelling	unlimited swelling	1287	992	612
Sulfur—3.0 Sulfenamide BT—1.2	unlimited swelling	unlimited swelling	1729	—	532

Another special feature of sulfenamide accelerators is that compared with
other accelerators, they show their effect at a much higher temperature. This
is proved by data obtained when determining the so called "initial vulcaniza-
tion temperature" (Table 3). By this is meant the beginning of an intense
period of vulcanization. The initial vulcanization temperature is the tempera-
ture at which (by determining the duration of vulcanization) the stock acquires
the ability of limited swelling.

The stocks under test were subjected to heating in an electric press for 40
minutes and at different temperatures from 100 to 130°, after which the swelling
was determined after 24 hours in xylene. From the data in Table 3, it can be
seen that when a mixture of MBTS and diphenylguanidine is present in the
vulcanization stock the mixture acquires the ability of limited swelling at a
temperature of 110°; in the presence of Sulfenamide BT limited swelling is
observed beginning at a temperature of 115°. Hence, when using Sulfenamide
BT the beginning of vulcanization shifts to an area of higher temperatures.

The special features previously described for the kinetics of vulcanization of
unfilled stocks, conditioned by the use of various accelerators, are also valid for
filled stocks. This can be seen from the data shown in Figure 5, which char-
acterize the kinetics of the vulcanization of tread stocks, containing 20 phr
channel black and 30 phr furnace black.
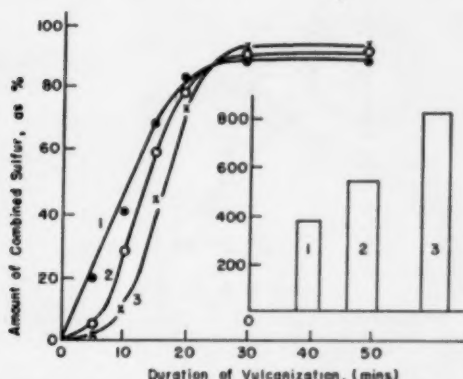
Fig. 5.—Comparison of the rate of sulfur combination (in tire tread stocks) with the bond strength of three-ply specimens. *1.* MBTS 0.5 phr; DPG 1.0 phr; *2.* Santocure 1.0 phr; *3.* Sulfenamide BT 1.0 phr.

It must be pointed out that in practice the course of vulcanization is normally judged by physical properties, in particular by the modulus. Stocks of SBR rubber are suitable for conducting physical tests as a rule after 15 to 20 minutes of vulcanization. The resulting data show the intensity of vulcanization at a much later stage in the process.

Figure 6 shows moduli with 300% elongation for the same stocks; the curves for combination of sulfur are shown in Figure 5. The data in Table 6 show that Sulfenamide BT after 20 to 50 minutes vulcanization guarantees higher moduli than when MBTS and DPG are used together. The rate curves for combination of sulfur prove convincingly that it does not, however, follow from this that after the first 20 minutes of vulcanization the action of Sulfenamide BT is more intense. It does prove that to explain the special feature of the course of vulcanization conditioned by using various accelerators we must not restrict ourselves to measuring the physical properties of stocks depending on the time of vulcanization.

The retarded rate of vulcanization in the initial stage of the process which is characteristic for sulfenamide accelerators is revealed by the fact that stocks
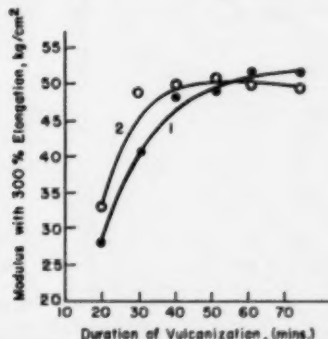
Fig. 6.—Rate of variation in modulus of tire tread stocks during vulcanization. *1.* MBTS 0.5 part by weight; DPG 1.0 part by weight; *2.* Sulfenamide BT 1.0 part by weight.
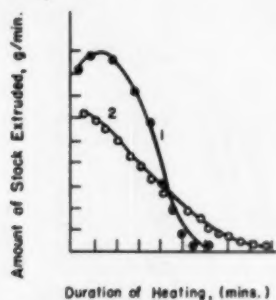
Fig. 7.—Variation in the viscoelastic properties of tire tread stocks at vulcanization temperature. 1. MBTS 0.5 part by weight; DPG 1.0 part by weight; 2. Sulfenamide BT 1.0 part by weight.

with these accelerators remain in a state of viscous flow for a much longer time. The variation in the flow of rubber stocks at vulcanization temperature, measured by their extrusion through a cylindrical aperture, proves this. From Figure 7 it can be seen that for tread rubber containing DPG and MBTS, complete loss of flow occurs after 12 minutes heating, while a stock with Sulfenamide BT, despite the fact that it has considerable initial rigidity, is in a state of viscous flow for 17 minutes.

The many experiments conducted show that systems characterized by the presence of an induction period of vulcanization, i.e., which remain in the state of viscous flow for a much longer period of time, have greater bond strength in multiply articles.

Figure 5 sets forth data on the resistance to dynamic ply separation of three layer specimens (tread—breaker strip—tread) with repeated shear. The breaker strip contained the same accelerators as the tread stock. Rubbers containing Sulfenamide BT in plied-up layers have resistance to dynamic ply separation almost one and a half times greater than rubbers with Santocure, and twice that of a rubber with DPG and MBTS.

Hence, with stocks containing the accelerators indicated a definite tendency was observed towards increased bond strength of multiply rubbers as the induction period of vulcanization was increased.

It is generally known that to intensify and increase the effect of vulcanization combinations of accelerators are widely used. Studies were made of the
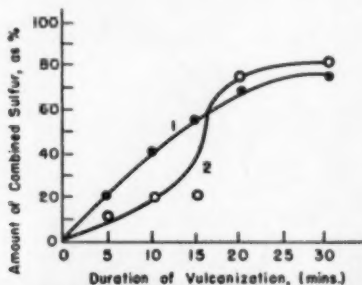
Fig. 8.—Rate of the combination of sulfur for unfilled stocks in the presence of TMTD (1) and in the presence of TMTD and MBTS (2).

TABLE 4

THE EFFECT OF MBTS ON THE SULFUR COMBINATION IN THE VULCANIZATION OF
TIRE TREAD STOCKS, CONTAINING TMTD

Composition of the vulcanizing system, phr	Cure time, min	Amount of sulfur reacted, %
Sulfur—1.7	10	60.0
TMTD—0.4	15	74.8
	20	76.8
Sulfur—1.7	10	40.8
TMTD—0.4	15	62.7
MBTS—1.0	20	73.9

course of the vulcanization of stocks of SBR rubber containing TMTD and
a combination of TMTD and MBTS. These studies showed that as the
MBTS was added to the TMTD there was a slowing up of vulcanization over
the first 10 to 15 minutes with a sharp increase in vulcanization rate subse-
quently. This is illustrated by data on the rate of the sulfur combination both
in unfilled (Figure 8) and filled (Table 4) stocks.

In unfilled stocks in the presence of 0.3 part by weight TMTD the amount
of reacted sulfur after 10 minutes vulcanization was 40%; with the same amount
of TMTD and 1.5 parts by weight MBTS the amount of sulfur did not exceed
20%. In filled stocks the amount of reacted sulfur for the time indicated was
60 and 40.8% respectively.

The decrease in the effect of vulcanization in the first stage of the process
which occurs as the MBTS is added to the thiuram mixture is shown con-
vincingly by the data obtained by swelling the stocks in benzene (Figure 9).
The amount of swelling of a vulcanizate after 10 minutes was 530%, while the
swelling of a vulcanizate using TMTD and MBTS was 800%. After 20 min-
utes vulcanization the stock containing TMTD and MBTS produces a much
greater vulcanization effect compared with stock containing TMTD alone.
In this case the maximum swelling of the first mixture was 410% and of the
second 480%.
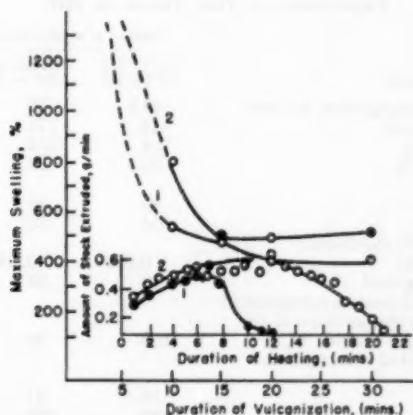
FIG. 9.—Rate of the variation in the viscoelastic properties of stocks and of the swelling of vulcanizates in benzene. 1. TMTD 0.3 phr; 2. TMTD 0.3 phr; MBTS 1.5 phr.
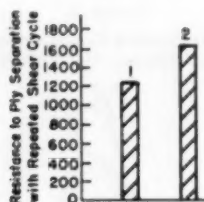
Fig. 10.—The effect of MBTS on the bond strength of plied-up rubbers containing channel black.
1. TMTD—0.3 phr; *2.* TMTD—0.3 phr: MBTS—1.5 phr.

The retarding effect of MBTS is clearly shown in the increased length of time the stock remains in a state of viscous flow at the vulcanization temperature of 143°. It was anticipated that this effect of MBTS would reflect favorably on the bond strength of plied-up rubbers. As can be seen from the data in Figure 10, when thiuram is replaced by an accelerating system consisting of TMTD plus MBTS, there is roughly a 30% increase in the resistance to dynamic ply separation of rubbers when subjected to repeated shear.

The experimental data therefore show that retarding vulcanization, with suitable physical properties attained as the optimum vulcanization is reached, results in a considerable increase in the monolithic nature of multiply articles.

One important factor in explaining the considerable increase in the bond strength of multiply rubbers when sulfenamide accelerators are used, in particular Sulfenamide BT is, in our opinion, the direct structurizing effect of this accelerator on the styrene-butadiene rubber. As we have already shown[1,2], this structurizing effect is the result of the polymerization processes of the rubber links of molecular chains which are activated by the sulfenamide accelerators. The vulcanizates prepared in the presence of sulfenamide accelerators contain, in addition to sulfur bonds, more stable —C—C— bonds. These endow the

TABLE 5

THE EFFECT OF SULFENAMIDE ACCELERATORS ON THE PHYSICAL
PROPERTIES OF TIRE TREAD OF SBR

Property	Content of accelerator, parts by weight		
	MBT—0.5 DPG—1.0	Sulfenamide BT—1.0	Santocure —1.0
Modulus with 300% elongation, kg/cm²	43.5	50	53
Tensile strength, kg/cm²	154	176	183
Specific elongation, %	752	752	728
Residual elongation, %	26	24.6	22
Elasticity			
at 20° C	45	49	49
at 100° C	48	52	53
Mechanical loss at 20° (coefficient of mechanical losses)	0.210	0.190	0.196
Dynamic modulus, kg/cm²	112	93	99
Heat formation with repeated compression and constant load (temperature of the specimen after 10,000 cycles), ° C	108	95	95
Resistance with repeated deformation, cycles × 10⁻³			
Compression	16	21	22
Flexing	135	180	180
Resistance to ply separation during repeated shear, cycles	382	834	550

vulcanizates with higher strength properties as well as increase the bond strength of plied-up rubbers.

The data in Table 5 show the effect of sulfenamide accelerators on the physical properties of vulcanized SBR. By replacing the accelerating system consisting of DPG and MBTS by Sulfenamide BT or Santocure, tensile strength and elasticity are considerably increased. Sulfenamide accelerators give vulcanizates good resistance to repeated deformation.

The physical properties of vulcanizates obtained with Sulfenamide BT and Santocure are practically identical except for the bond strength of multiply rubbers. Plied-up rubbers prepared using Santocure are superior in their resistance to ply separation to rubbers obtained using MBTS and DPG, but are inferior to those prepared with Sulfenamide BT.

The good effect of Sulfenamide BT on the physical properties of vulcanized SBR (including the bond strength of multilayer articles) can be confirmed, as was convincingly done so in the report of G. N. Buiko et al.[3] by the plurality of data obtained from exhaustive bench and road tests of tire casing. In particular the test carried out in collaboration with the chemico-technological section of the Scientific Research Institute of the Tire Industry on manufacturing 7.50–20 tires completely from SKS-30 using Sulfenamide BT in one batch and DPG and MBTS in the other, showed that tires manufactured from stocks vulcanized using Sulfenamide BT had much greater life.

The experimental data therefore prove that the considerable increase in bond strength obtained using sulfenamide accelerators can be explained by (1) the slowing up in the rate of vulcanization in the initial stage of the process, resulting in the stocks remaining longer in a state of viscous flow, and (2) the formation of more stable crosslinks which results in the vulcanizates having greater static and dynamic strength.

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THE CROSSLINKS IN TMTD–ZINC OXIDE–NATURAL RUBBER VULCANIZATES *

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The mechanism of vulcanization of natural rubber (NR) by means of tetra-methylthiuram disulfide (TMTD) and zinc oxide has been the subject of much recent experimental work and speculation[1-3]. While such studies have clarified the kinetics and stoichiometry of TMTD decomposition and zinc dimethyldi-thiocarbamate formation[3], they have not directly aided our knowledge of the nature of the crosslinks in the resultant vulcanizate. It was earlier suggested that the vulcanizate contained only C—C crosslinks[4], comparable with those formed by means of di-*tert*-alkyl (and aralkyl) peroxides[5, 6], while more recently, disulfide crosslinks have been proposed[3]. However, neither of these views has been confirmed by direct chemical studies of the vulcanizate. Evidence is now presented which shows that there can be no appreciable amount of C—C cross-linking by the TMTD-ZnO combination, and this is consistent with the view that sulfur crosslinks predominate. This conclusion is based on the respective swelling properties in *n*-decane of dicumyl peroxide vulcanizates (containing only C—C crosslinks) and TMTD-ZnO vulcanizates, which have been treated with methyl iodide *in vacuo* at 80° C. This reagent is known to cause the fission of C—S and S—S bonds in variously constituted organic mono- and polysulf-ides[7] and should therefore cause the fission of sulfur crosslinks in a vulcanizate with consequent degradation of the network (cf. Ref. 8), whereas there is no evidence that di-allylic C—C crosslinks can be similarly degraded.

Details of the vulcanizing mixes and the vulcanization conditions used are as follows:

(*1*) *TMTD-ZnO vulcanizate.*—A mix comprising smoked sheet NR (100 parts) ([η], 2.29 (g./100 ml)$^{-1}$ in benzene at 25° C); TMTD (4 parts, 1.66 × 10^{-4} mole/g rubber); and zinc oxide (4 parts) was vulcanized for 120 min at 140° C, conditions leading to maximum degree of crosslinking. The vulcani-zate was extracted with boiling acetone for 24 hr in nitrogen in the dark and then dried *in vacuo* (<10^{-5} mm) at room temperature [Found: Organically combined S, 0.43%, determined by oxidation with nitric acid-perchloric acid and turbidimetric estimation of sulfate ion as barium sulfate; inorganic sulfide S, 0.01%; ash (mainly ZnO), 3.65%].

(*2*) *Dicumyl peroxide vulcanizate.*—A mix comprising NR (100 parts) ([η], 2.64 (g/100 ml)$^{-1}$) and the peroxide (3 parts) was vulcanized for 90 min at 140° C, and the vulcanizate extracted and dried as for (*1*) above.

Samples of the vulcanizates together with redistilled methyl iodide were sealed *in vacuo* (<10^{-5} mm), using the technique previously described for the quantitative determination of crosslinking in peroxide vulcanizates[6], and the samples were then heated in the dark as detailed in Table I. As controls, samples of the vulcanizates were similarly treated in the absence of methyl-

TABLE I
DEGREE OF CROSSLINKING OF VULCANIZATES BEFORE AND AFTER TREATMENT WITH METHYL IODIDE

Expt. No.	Methyl iodide (g/g vulcanizate)	Reaction conditions (in vacuo, $<10^{-4}$ mm)	% gel[a]	w of gel[b]	$1/2M_c^a$, phys. ($\times 10^4$)	$1/2M_c^a$, chem. ($\times 10^4$)	$1/2M_c^a$, chem. ($\times 10^4$)
			TMTD–ZnO–NR Vulcanizate				
1	—	—	100	0.284	0.96	0.53	0.46
2	—	121 hr. at 80° C	100	0.284	0.96	0.53	0.46
3	1.96	121 hr. at 80°	94	0.0485	0.26[c]	0.085	0.072
4	—	336 hr. at 80°	100	0.284	0.96	0.53	0.46
5	1.95	336 hr. at 80°	77	0.308	—	—	—
6	—	594 hr. at 25°	100	0.284	0.96	0.53	0.46
7	1.95	594 hr. at 25°	99	0.163	0.45	0.16	0.12
8	—	24 hr. at 140°	100	0.271	0.88	0.465	0.39
9	1.96	24 hr. at 140°	63	0.153	—	—	—
			Dicumyl Peroxide Vulcanizate				
10	—	—	100	0.307	1.09	0.63	0.59
11	—	121 hr. at 80°	100	0.307	1.09	0.63	0.59
12	1.96	121 hr. at 80°	100	0.299	1.04	0.59	0.54
13	—	24 hr. at 140°	100	0.312	1.13	0.66	0.62
14	1.96	24 hr. at 140°	99	0.541	—	—	—

[a] Wt. % of vulcanizate insoluble in n-decane after 48 hr swelling at 25.0° C. [b] Equilibrium volume fraction of rubber in swollen gel; corrections applied for nonrubber components of the vulcanizate. [c] Based on extrapolated value of M_c, phys., since w value is outside experimental range of previous calibration[14].

iodide. After reaction, excess methyl iodide was removed *in vacuo* at room temperature and the degree of crosslinking of the vulcanizates determined by measuring the equilibrium volume swelling, v_r, in *n*-decane at 25° C. (cf. Ref. 6). Use of the v_r values, the estimated number average molecular weight of the rubber ($\bar{M}_n$) prior to vulcanization, and the methods of Mullins[9], and Moore and Watson[6], yield values of the degree of "physical" and "chemical" crosslinking, $1/2M_{c,\,phys.}^{\infty}$ and $1/2M_{c,\,chem.}^{\infty}$ mole/g rubber hydrocarbon, respectively, for vulcanizates derived from rubbers having infinite $\bar{M}_n$ prior to vulcanization. The data are given in Table I, which also include values of $1/2M_{c,\,chem.}^{\infty\,*}$ based on a revised and somewhat improved form[10] of the original calibration[6] relating the physical to chemical degree of crosslinking. The observed difference between these latter two values has been attributed to the entanglement contribution to the elastically effective network[6].

Treatment of the TMTD-ZnO vulcanizate with methyl iodide at 80° C (Expt. 3) leads to extensive degradation of the network, approximately 85% of the chemically introduced crosslinks being destroyed, based on the values of $1/2M_{c,\,chem.}^{\infty\,*}$ of the original and treated vulcanizates. Comparable treatment of the peroxide vulcanizate (Expt. 12) destroyed only ca. 8.5% of the original (C—C) crosslinks. The control experiments (expts. 2 and 11) show that there is no purely thermal degradation of the networks under the conditions used. Attempts to completely degrade the TMTD-ZnO network by reaction with methyl iodide at 80° C for an extensive period (Expt. 5) or at 140° C (Expt. 9) were not successful, since crosslinking and other network modifictions of unknown type compete with the degradative reaction of the methyl iodide to give a gel component which is hard, brittle, and inelastic. (Crosslinking of the peroxide vulcanizate also results from treatment with methyl iodide at 140° C; Expt. 14). Use of a lower temperature (25° C, Expt. 7) to avoid the competitive crosslinking reaction again did not effect complete degradation of the TMTD-ZnO vulcanizate, although ca. 74% of the intial chemical crosslinks were destroyed under these conditions.

The above evidence, in conjunction with the anticipated mode of action of methyl iodide on C—S—C, C—S_x—C, and C—C crosslinks, indicates that a TMTD-ZnO vulcanizate must contain mainly, or possibly entirely, sulfur containing crosslinks. This conclusion is supported by the fact that sulfuration of a simple mono-olefin with TMTD-ZnO at 140° C yields mainly di-alkenyl mono- and disulfides, but no products resulting from C—C crosslinking of the olefin[11]. The reaction of methyl iodide with organic mono- and polysulfides is not sufficiently specific to determine precisely the nature of the sulfurated crosslinks (i.e., structure of the hydrocarbon units at the crosslink and the length of the sulfur chains) in TMTD-ZnO vulcanizates, and this is to be sought by further studies with olefinic models for NR.

The present data also yield information about the stoichiometry of crosslinking by the TMTD-ZnO combination at 140° C. Since the vulcanizate studied here was prepared under conditions leading to maximum crosslinking, it is reasonable to assume complete decomposition of the TMTD and of an intermediate formed by interaction of the TMTD with the rubber hydrocarbon. The formation of this intermediate and its subsequent decomposition to yield zinc dimethyldithiocarbamate and crosslinks is suggested by the work[12] of Scheele et al., and of Dunn and Scanlan[13]. Using the value of $1/2M_{c,\,chem.}^{\infty\,*}$ for the original extracted vulcanizate (Expt. 1), it is calculated that 3.6 molecules of TMTD are required to produce one chemical crosslink and that 3.0 atoms of sulfur are combined in the network for each chemical crosslink formed.

These values agree reasonably well with the respective figures of 3.8 moles TMTD decomposed and 1.9 atoms of sulfur combined per crosslink, obtained recently by Bevilacqua[14] by a less direct method. It is not to be inferred from the present results that the crosslinks in a TMTD–ZnO–NR vulcanizate contain, on the average, 3 sulfur atoms, since some of the combined sulfur may be attached to the main polymer chains as sulfurated residues from the TMTD. They do, however, establish the sulfurated nature of the crosslink and confirm the high crosslinking efficiency of TMTD and ZnO as compared with unaccelerated sulfur–NR and conventional mercaptobenzothiazole-sulfur–NR systems at 140° C which require, respectively, ca. 30 and ca. 12 sulfur atoms combined in the network per chemical crosslink formed[15].

I wish to thank Mr. L. Mullins and Dr. J. Scanlan for their cooperation and advice, and Mr. B. R. Trego for experimental assistance during the course of this work.

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THE REACTION OF TETRAMETHYLTHIURAM
DISULFIDE AND MONOSULFIDE
WITH RUBBER *

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The analyses of extracted vulcanizates in several laboratories[1] have established that sulfur and nitrogen containing fragments from TMTD (tetramethylthiuram disulfide) add to rubber molecules during vulcanization with this reagent. Simultaneously, as shown by us, TMTD is reduced to dimethyldithiocarbamic acid which is found in the form of the zinc dithiocarbamate in mixtures resulting from reaction with zinc oxide or zinc stearate. The acid decomposes into carbon disulfide and dimethylamine in mixtures not containing metal oxides or salts such as those of Zn, Mg, or Ca. In the case of decomposition of this acid there is noted a "reversion" of vulcanization and the vulcanizates possess worse mechanical properties than do those vulcanizates obtained when zinc oxide is also present.
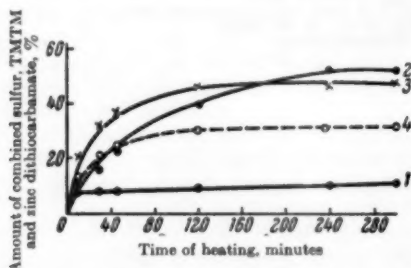
Fig. 1.—Kinetics of interaction of TMTM with natural rubber. Curve 1, S combined/S added in %, mixture: 3.5 phr TMTM and 1 phr PBNA (phenyl-2-naphthylamine); 2, S combined/S added in %, mixture: 3.5 phr TMTM, 5 phr zinc oxide and 1 phr PBNA; 3, zinc dithiocarbamate in mole % from addition of TMTM (mixture the same); 4, sulfur in the form of zinc dithiocarbamate (1 mole of dithiocarbamate from two moles of TMTM, mixture the same).

Certain investigators presume the formation of TMTM in the process of vulcanization by the disulfide[2]. In this connection it was of interest to examine the interaction of TMTM (tetramethylthiuram monosulfide) with rubber. No effect of vulcanization during hearing of mixtures of natural and synthetic polyisoprene rubber with TMTM (with and without zinc oxide) in a press at 143–175° is noted. Having obtained products completely soluble in xylene and not having a finite modulus of elasticity shows the absence of crosslinks between molecules of rubber. By qualitative reactions it was established that during heating of these mixtures there was formed tetramethylthiourea (not

detected in vulcanization with TMTD) and carbon disulfide, and, in the absence of zinc oxide, more carbon disulfide and dimethylamine.   Consequently, along with its interaction with rubber, TMTD undergoes thermal degradation which is absent in the case of TMTM[3].   In the process of heating, mixtures of TMTM and zinc oxide react to form zinc dimethyl dithiocarbamate[4].   Kinetics of the combination of sulfur from TMTM in a mixture with zinc oxide differ from kinetics of combination of it in the absence of zinc oxide (Figure 1).   In the last case there is combined up to 10% sulfur (from the addition in the form of TMTM) and with zinc oxide—up to 50% and, moreover, here there is formed somewhat more than 50 mole % zinc dithiocarbamate from the addition of TMTM.   In mixtures with TMTD the amount of combined sulfur in the presence and absence of zinc oxide is practically the same.   The maximum in the kinetic curves for sulfur combination, typical for mixtures with TMTD, is absent in the case of TMTM.
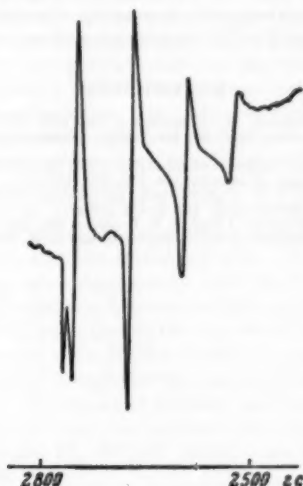
FIG. 2.—Electron paramagnetic resonance spectrum of mixture of 100 parts of natural rubber and 3 parts of TMTD, heated for 10 minutes at 140°.   The abscissa reads in gauss.

For examination of the character of interaction between rubber, TMTD and TMTM the electronic paramagnetic resonance[5] spectra in process of heated mixtures containing TMTD and TMTM were investigated.   Investigations of four mixtures, containing per 100 parts of acetone extracted natural rubber: 1) 3 parts of TMTD; 2) 3 parts of TMTD and 5 parts of zinc oxide; 3) 10 parts of TMTD; 4) 10 parts of TMTM.   Mixtures were prepared on microrolls in an argon atmosphere and placed in quartz ampules, which were heated immediately in a resonance chamber (in argon, vacuum and air).   During heating of all mixtures (140°) there appeared essentially the same spectrum (Figure 2), the least intense being in the mixture with TMTM.   This shows that the mechanism of interaction of TMTD and TMTM with rubber, most likely, is the same, whereas kinetic principles distinguish them very significantly.   Corroboration of this appears in the reaction of TMTD and TMTM with geraniol, which one may examine in character as a model structural unit for natural

rubber.   During heating of mixtures of TMTD and TMTM with geraniol, and also during irradiation of them in a quartz ampule by ultraviolet light, they acquire the same red-orange color, the intensity of which increases more slowly in the mixture with TMTM.

The stated facts allow us to infer that TMTM, as well as TMTD[1, 2], interacts with rubber through the stage of free radicals, the disintegration of this structure taking place along the C—S and S—S bond[3, 4].

SUMMARY

The kinetics of the reaction of tetramethylthiuram monosulfide (TMTM) differ from that with the disulfide (TMTD).   No formation of chemical crosslinks takes place; the sulfur of TMTD adds in correspondence with a curve exhibiting no maximum and the addition differs in the presence and absence of zinc oxide. Simultaneously, the thermal decomposition of TMTM takes place.   The electron paramagnetic resonance spectra and the reaction with geraniol show TMTD and TMTM to interact with rubber through a free radical stage.

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THE INTERACTION OF TETRAMETHYLTHIURAM DISULFIDE WITH RUBBER AND WITH COMPOUNDS CONTAINING A LABILE HYDROGEN ATOM *

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In our preceding work a series of questions were posed about thiuram vulcanization in the presence of various metal oxides[1]. Various points of view exist with respect to the mechanism of the vulcanizing action of the thiuram sulfides. One group of investigators[2] considers that the vulcanizing action of these accelerators is explained by the discharge of active sulfur with parallel degradation to simpler compounds. In other works[3] there is developed a concept of thiuram vulcanization as a free radical process.

In works of Scheele and others there is evidence that during vulcanization in the presence of zinc oxide thiuram is transformed into 66.6 mole % of zinc dithiocarbamate; any other products of its transformation are absent. According to the authors the idea of the formation of an intermediate compound involving thiuram, rubber, and the surface of zinc oxide crystals is developed. The intermediate decomposes subsequently with the formation of zinc dithiocarbamate and chemical crosslinks between rubber molecules[4]. These authors do not consider thiuram vulcanization in the absence of metal oxides and neither do they present experimental data on the primary interaction of thiuram with rubber. In this same trend of thought in the journal, *Visokomolekularnye Soedineniya*, there was quoted a statement of Scheele and Hummel which dealt with this question. (It is believed that the authors here refer to Scheele and Hummel, *Kautschuk und Gummi* 11, WT267 (1958); see also RUBBER CHEM. & TECHNOL. 32, 566 (1959). *Ed.*)

INTERACTION OF TETRAMETHYLTHIURAM DISULFIDE (TMTD) WITH RUBBER

Tetramethylthiuram disulfide (TMTD) in conventional vulcanization (at 143° in a press) adds chemically to rubber which can be detected by the presence of sulfur and nitrogen (after extraction by hot and cold acetone, cold ethyl acetate or boiling alcohol. The kinetics of addition of sulfur and nitrogen from TMTD to rubber is shown in Figure 1. In our own work[1] on the kinetic curves characterizing the bound sulfur in vulcanization we show that there is clearly a pronounced maximum. The explanation of this interesting phenomenon will be given below.

As was expressed by one of us[5] the process goes rather apparently by way of formation of free radicals from TMTD which interact with the rubber molecules and which stimulate a polymerization action similar to that which occurs in the case of benzothiazolyl disulfide (MBTS).

Unequal amounts of combined sulfur and nitrogen (in per cent of the original content in TMTD) (cf. Figure 1) show that both symmetrical and unsymmetrical decomposition of TMTD occurs according to the scheme:

$$(CH_3)_2N—C—S—S—C—N(CH_3)_2 \rightleftharpoons 2(CH_3)_2N—C—S\cdot$$
$$\underset{S}{\|} \quad \underset{S}{\|} \qquad\qquad I \qquad \underset{S}{\|}$$

$$\longrightarrow (CH_3)_2N—C—S—S\cdot + \cdot C—N(CH_3)_2$$
$$\underset{S}{\|} \qquad\qquad \underset{S}{\|}$$
$$II \qquad\qquad III$$
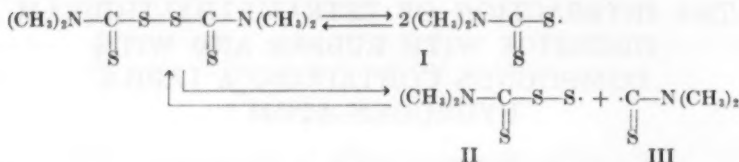
Upon the removal of the labile hydrogen atom found in the α-position to the double bond of the rubber molecule by radicals (I) and (II) there is formed dithiocarbamic acid which is either decomposed to carbon disulfide and amine or is bound in the form of dithiocarbamate.   The stabilization of reaction products (dithiocarbamates) is observed in the presence of zinc oxide, lead oxide (PbO) and nickel oxide (NiO); decomposition occurs in the absence of oxide and in the presence of magnesium and calcium oxides.   The stearates of these two metals
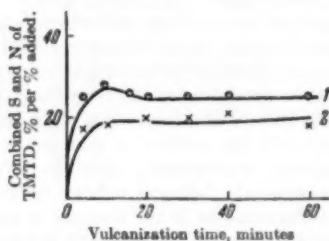
Fig. 1.—Combined sulfur (Curve *1*) and nitrogen (Curve *2*) of TMTD (in % per % added) in vulcanization of synthetic polyisoprene rubber (SKI).   Composition of stock in phr: TMTD—5, ZnO—5, stearic acid—1.

behave in a fashion analogous to the oxides.   The behavior of lead and nickel oxides should especially be noted.   During the heating of rubber at vulcanization temperatures with three parts of TMTD and an amount of PbO and NiO equivalent to five parts of zinc oxide crosslinks are not formed—the "vulcanizates" are completely soluble in xylene.   The sulfur content in extracted samples differs little from the total sulfur content and from the sulfur added as thiuram (85–90%).   Extraction was accomplished with cold and with boiling ethyl acetate and hot acetone, i.e. substances in which lead and nickel dimethyl- and diethyldithiocarbamates readily dissolve.   It is possible, therefore, to consider that lead and nickel dithiocarbamates are found in rubber in bound form (possibly in the form of complex compounds).   In vulcanizates from commercial synthetic polyisoprene rubber the extent of crosslinking in the presence of these oxides is less than in the absence of metal oxides and, furthermore, the extent of crosslinking becomes less with increasing quantity of lead or nickel oxides. These facts indicate that bonding of products of reaction of TMTD with rubber by lead and nickel oxides occurs during simultaneous addition of these metal dithiocarbamates to molecular chains of rubber at the sites of reaction with TMTD.

Zinc dithiocarbamate (ZnDTC) is found in rubber in the dissolved state

and may be removed by extraction.   In vulcanizates without metal oxides or
in those containing magnesium and calcium oxides the binding of dithiocar-
bamic acid does not occur and it decomposes into carbon disulfide and di-
methylamine.   Both of these compounds were detected by qualitative reactions
for each separately and conjointly (formation of a brown precipitate of copper
dimethyldithiocarbamate on addition of a solution of $CuSO_4$ to an aqueous
extract of the vulcanizate).   Moreover, there was observed a significant de-
crease in the quantity of total sulfur in the vulcanizates due to evolution of
carbon disulfide.   A mixture of natural rubber and TMTD was heated in the
absence of metal oxides *in vacuo* and the dimethylamine in the volatile products
was determined quantitatively (absorption by 0.1 N HCl with subsequent
titration of the excess by 0.1 N NaOH).   During this operation part of the
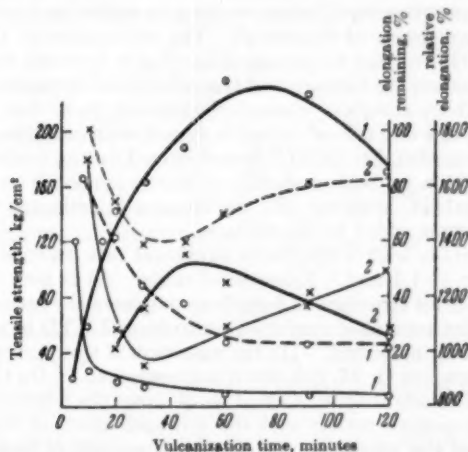
Fig. 2.—Physical properties of vulcanizates of SKI with TMTD.   Composition of mixture (in parts)e
1—SKI 100, TMTD 3, ZnO 1, PBNA 1.   *2*—SKI 100, TMTD 3, MgO 0.5, PBNA 1.   ———— tensile
strength, ———— relative elongation, - - - - remaining elongation.

dimethylamine reacts with carbon disulfide at the walls of the condenser in the
process of volatilization with the formation of dimethylammonium dimethyl-
dithiocarbamate.

$$(CH_3)_2N-C-SH-NH_2(CH_3)_2$$
$$\overset{\|}{S}$$
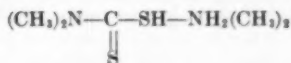
In the presence of zinc oxide (or zinc stearate) there is observed a three
dimensional network (in contrast with other metal oxides) and reversion is
absent.   The physical properties of vulcanizates from polyisoprene rubber and
zinc oxide are considerably better than those of vulcanizates obtained with
equivalent amounts of magnesium oxide (Figure 2).

Thus, the particular character of zinc oxide among the several metal oxides
studied during thiuram vulcanization may be explained by the formation of the
zinc salt of dithiocarbamic acid which is sufficiently stable under conditions of
vulcanization and does not interact with rubber.   Kinetics of its accumulation
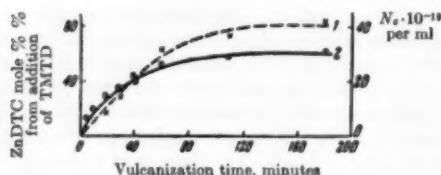
FIG. 3.—Formation of crosslinks (*1*) and zinc dithiocarbamate (*2*) in process of vulcanization of rubber with TMTD. Composition of the mixture: natural rubber (extracted with cold acetone in a stream of N₂ for 50 hours)—100, TMTD–4, ZnO—5, PBNA—1.

are shown in Figure 3. ZnDTC was determined in alcohol extracts of the vulcanizates by conductimetric titration methods[3]. The number of crosslinks was determined by measuring equilibrium swelling in xylene and calculating with the help of a monograph of Schwartz[6]. The calculation of the number of molecules of ZnDTC related to one crosslink (Table 1) shows that in the first period of vulcanization the formation of this compound surpasses the formation of crosslinks. Thus, complete characterization of these two reactions, as considered by Scheele and others[4], is not in accord with our data.

It should be recorded that ZnDTC is not formed during milling of mixtures or extraction of them by boiling alcohol (2 hours) inasmuch as in extracts of crude mixtures ZnDTC is absent and the amount of extracted TMTD corresponds to the amount added to the mixture.

Reaction of rubber with TMTD at a significant rate depends upon the proportion in rubber of 1,4 and 1,2 structural units. As is seen from Figure 4 with an increase of 1,4 structure in butadiene polymers the rate of crosslinking is increased and the amount of combined sulfur from TMTD in mixtures of the same composition is diminished. (In the execution of this part of the work the participation of student G. M. Sokolov is acknowledged.) On the basis of this it is possible to conclude that the formation of crosslinks depends on the interaction of thiuram radicals mainly with the hydrogen atoms in the α-position to the double bond of the 1,4 structure. The large amount of bound sulfur from TMTD in rubbers with a large amount of 1,2 units may be explained by combination of radicals of TMTD to sidechain groups. This process does not cause formation of crosslinks since saturation of the double bonds occurs. Therefore, it was of interest to follow the kinetics of the accumulation of ZnDTC in rubbers with different percentages of structural units (Figure 5). More rapid formation of ZnDTC in rubbers with a large amount of 1,2 structure appears somewhat unexpectedly. This fact points to the possibility of formation of dithiocarbamic acid during removal of hydrogen at *tertiary* carbon atoms by radicals of

TABLE 1

FORMATION OF CROSSLINKS AND ZNDTC DURING VULCANIZATION OF NATURAL RUBBER WITH TMTD IN THE PRESENCE OF ZNO

Vulcanization time, minutes	Number of crosslinks $N_c \times 10^{-19} ml^{-1}$	Number of molecules of ZnDTC, $n \times 10^{-19}$	Number of molecules of ZnDTC for each crosslink
20	0.84	2.5	3
30	1.66	2.9	1.7
60	3.61	5.1	1.4
110	3.27	5.3	1.6
120	4.25	5.4	1.3

TMTD with the formation of active polymer radicals. In this radical pendant vinyl groups are situated sufficiently near to one another so that, as a consequence of interaction between them, these sections of molecular chains will be rigid. All this makes more probable the saturation of radicals of the type

$$-CH_2-C-CH_2-CH-$$
$$\underset{CH_2}{\overset{CH}{\|}} \qquad \underset{CH_2}{\overset{CH}{\|}}$$
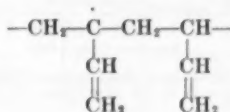
by the remnants of TMTD than participation of them in crosslinking.

In this way the amount of sulfur of TMTD combined to rubber is determined by the type of rubber and not the metal oxide. In the presence of vari-
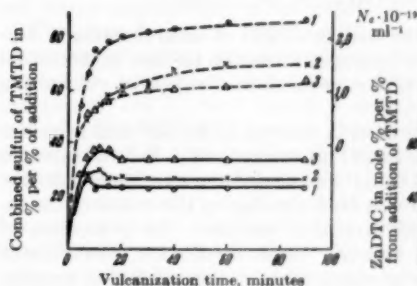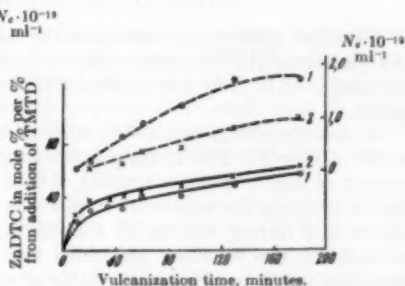
FIG. 4.—Combined sulfur from TMTD (in % from addition) and formation of crosslinks (N_c) during vulcanization of rubbers with different structural units: 1,4 and 1,2. —— $\dfrac{S_{combined}}{S_{added}}$; - - - N_c. Composition of the mixture (parts): rubber—100, TMTD—4, ZnO—5, stearic acid—2, PBNA—1. Curve *1*—natural rubber (100% 1,4 bonds), *2*—SKBM (65% 1,4 bonds), *3*—SKB (30% 1,4 bonds). (Proportion of structural units determined chemically by H. G. Samsonov.)

FIG. 5.—Formation of crosslinks (N_c) and accumulation of zinc dithiocarbamate during vulcanization of synthetic polyisoprene rubber with different proportions of 1,2 and 1,4 units. Curve *1*—polyisoprene (94% 1,4 structure), *2*—polyisoprene (86% 1,2 and 3,4 structures). —— ZnDTC; - - - N_c. Composition of the mixture (parts): rubber—100, TMTD—3, ZnO—5. (Proportion of structural units were determined with the help of infrared spectra in VNIISK.)

ous metal oxides the quantity limits of combined sulfur of TMTD vary little for a given rubber (22–27% in the case of natural rubber).

Moreover, the relative amount of combined sulfur from TMTD is almost independent of the amount of added TMTD or metal oxide.

It is evident that the metal salt or oxide plays an essential role in binding reaction of products TMTD with rubber and one or the other is important for the formation of three dimensional vulcanizate networks. In this reaction there is no essential difference between metal oxide and stearate. This shows that the crystal structure of zinc oxide has little significance with respect to the formation of technically useful thiuram vulcanizates[4]. The latter effect is confirmed further by the fact that from synthetic polyisoprene rubber with ten parts by weight of TMTD without zinc oxide it is possible to obtain vulcanizates with almost an equal number of crosslinks as in vulcanizates with four parts by weight of TMTD and five parts by weight of zinc oxide. Vulcanizate mixtures
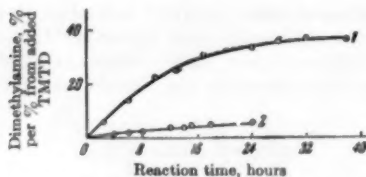
FIG. 6.—Kinetics of evolution of dimethylamine during reaction of TMTD with geraniol in xylene solution at 136°. *1*—0.3 g TMTD, 12 ml geraniol in 100 ml o-xylene. *2*—0.3 g TMTD in 100 ml o-xylene.

from natural rubber with ten parts by weight of TMTD without zinc oxide possess satisfactory mechanical properties[2].

REACTION OF TMTD WITH GERANIOL AND ISOPROPYLBENZENE THERMAL DECOMPOSITION OF TMTD

We chose geraniol as a model of the structural unit of natural rubber. Isopropylbenzene (IPB) contains a labile hydrogen atom at a tertiary carbon atom and also is of interest for the study of the mechanism of action of vulcanizing agents.

Reactions with geraniol were conducted in mineral oil at 143° and in xylene at 136° (0.3 g TMTD, 12 ml geraniol in 100 ml of solution). Before heating, a current of argon (oxygen content, 0.05%) was passed for two hours into the flask containing the mixture. Argon was used also during the course of the reaction and during cooling of the mixture after reaction. In a medium of mineral oil the reaction proceeded slowly. Upon distillation, the volatile materials were identified as the same products that are formed during reaction with rubber under similar conditions. Significantly, the reaction proceeds rapidly in xylene (Figure 6). There is noted a marked evolution of amine during heating of TMTD in xylene and, in the absence of geraniol, dimethylamine is not detected during heating of TMTD in mineral oil for five hours. The product of reaction of TMTD with geraniol has a bright red-orange color. Also the color of the reaction mixture appears during exposure in a quartz
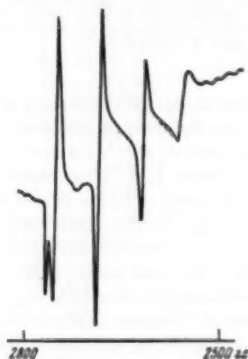
FIG. 7.—EPR spectrum of a mixture of 100 parts natural rubber with 3 of TMTD after heating for 10 minutes at 140°C.

ampule at room temperature to ultraviolet light from a mercury lamp SVDSH. It is possible to consider this fact as an indication that the reaction proceeds through a free radical stage.

The reaction of TMTD with IPB (0.1 g of TMTD in 50 ml IPB) was conducted under similar conditions (50 minutes at 136°). After the reaction the IPB was distilled off *in vacuo* and the residue was dissolved in 50 ml of acetone. The amount of unreacted TMTD (determined by conductimetric titration with 0.1 N $CuSO_4$ in the presence of hydroquinone) constitutes 61 mole % of the amount added. In the presence of zinc oxide ZnDTC is formed; however, because of the poor dispersion of zinc oxide in the solution, dithiocarbamic acid is partly degraded as discussed in regard to the formation of dimethylamine.

In this way TMTD reacts both with rubber and with the indicated low molecular weight compounds containing a labile hydrogen atom to form the same products. The essentially thermal degradation of TMTD under these conditions does not occur; in the vulcanizate only traces of zinc sulfide are found and tetramethylthiourea is not found.

The degradation of TMTD with the formation of thiuram monosulfide, tetramethylthiourea, carbon disulfide and sulfur occurs during heating in the absence of compounds containing a labile hydrogen atom. Thus, weighed amounts of TMTD were heated in sealed ampules in air and argon in an oil bath at 143° for 1.5 to 2 hours. During this heating the formation of a dark-yellow fluid and, after cooling, the formation of light yellow crystals of tetramethylthiuram monosulfide (TMTM) (m.p. 106°) is observed.

In a water extract of the contents of the ampules after heating tetramethylthiourea was found as judged by the formation of a yellow strain[7] in the solution when Bi^{3+} and carbon disulfide were added and by the formation of a grey-brown precipitate when an aqueous solution of $CuSO_4$ and diethylamine was added. Consequently, during thermal degradation of TMTD dimethylamine is not formed. Qualitatively, elemental sulfur was found as judged by the blue color at the interface of the acetone and concentrated KOH solution[8]. TMTM under the same conditions is degraded with the formation of tetramethylthiourea and carbon disulfide.

DISCUSSION

The stated facts show that the interaction of TMTD with rubber goes by participation of free radicals without extreme thermal degradation of them as was shown in the first paper of Scheele and coworkers[2]. In the absence of compounds with a labile hydrogen atom the thermal degradation of TMTD proceeds with the formation of thiuram monosulfide, tetramethylthiourea, carbon disulfide and sulfur.

Guryanova and Kuzhina[9] showed that isotopic exchange of TMTD with elemental sulfur goes by a free radical mechanism. They consider the possibility of cleavage into radicals at the C—S bond with the formation of radicals (II) and (III) since this bond must be broken in order to exchange the sulfur atom of the C—S group. Therefore, it seems entirely likely that such a pattern of behavior occurs during vulcanization.

The interaction of TMTD with rubber (RH) and with other compounds with a labile hydrogen atom proceeds apparently in the following way: Radicals (I) and (II) may react with double bonds or accept hydrogen to form the unstable dithiocarbamic acid. Radical (III) in all probability is added to the new

polymer radicals which form. Thus, during symmetrical cleavage of TMTD into radicals the process may go according to the scheme:

$$(CH_3)_2N-\overset{\underset{\|}{S}}{C}-S\cdot \xrightarrow{+\ RH} R\cdot +\ (CH_3)_2N-\overset{\underset{\|}{S}}{C}-SH \xrightarrow{ZnO} ZnDTC +\ H_2O$$

$$(CH_3)_2N\overset{.}{H} +\ CS_2$$

$$(CH_3)_2N\overset{\underset{\|}{S}}{C}-SH-NH(CH_3)_2$$
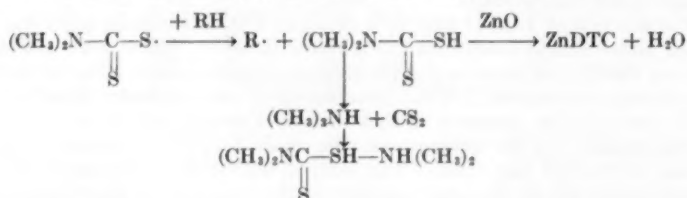
During unsymmetrical cleavage the process goes according to the scheme:

$$(CH_3)_2N-\overset{\underset{\|}{S}}{C}-S-S\cdot \xrightarrow{+\ RH} RS\cdot +\ (CH_3)_2N\overset{\underset{\|}{S}}{C}-SH$$
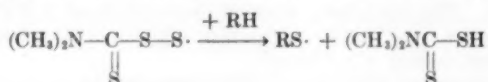
and then proceeds as in the preceding scheme.

Radicals R· and RS· may either add to one another or to a rubber molecule to form a crosslink in the vulcanizate or may be saturated by radicals (I) or (III). The existence of a limiting amount of combined sulfur from TMTD (22–25% in the case of natural and synthetic polyisoprene rubbers), the decomposition of dithiocarbamic acid and the formation of ZnDTC (56 mole %) is explained, apparently, by the existence of a definite proportion of symmetrical and unsymmetrical cleavage of TMTD into radicals.

According to the foregoing scheme, thiuram vulcanizates must form C—C or C—S—C crosslinks mainly and an insignificant number of C—S—S—C crosslinks which agrees with the data of Dogadkin and Tarasova[10] concerning stress relaxation rate and rate of isotope interchange of thiuram vulcanizates with elemental sulfur[10].

In the absence of compounds with a labile hydrogen atom, radicals of TMTD formed during heating undergo further, more extreme degradation. Products of thermal degradation which we identified allow us to represent this process in the following manner:

$$(CH_3)_2N-\overset{\underset{\|}{S}}{C}-S-S\cdot \longrightarrow (CH_3)_2N-\overset{\underset{\|}{S}}{C}-S\cdot +\cdot S\cdot \xrightarrow{+\ (CH_3)_2N-\overset{\underset{\|}{S}}{C}\cdot}$$

$$\longrightarrow (CH_3)_2N-\overset{\underset{\|}{S}}{C}-S-\overset{\underset{\|}{S}}{C}-N(CH_3)_2 +\ elemental\ sulfur;$$

$$(CH_3)_2N-\overset{\underset{\|}{S}}{C}-S\cdot \longrightarrow (CH_3)_2N\cdot$$

$$+\ (CH_3)_2N-\overset{\underset{\|}{S}}{C}\cdot$$

$$+\ CS_2 \longrightarrow (CH_3)_2N-\overset{\underset{\|}{S}}{C}-N(CH_3)_2 +\ CS_2$$
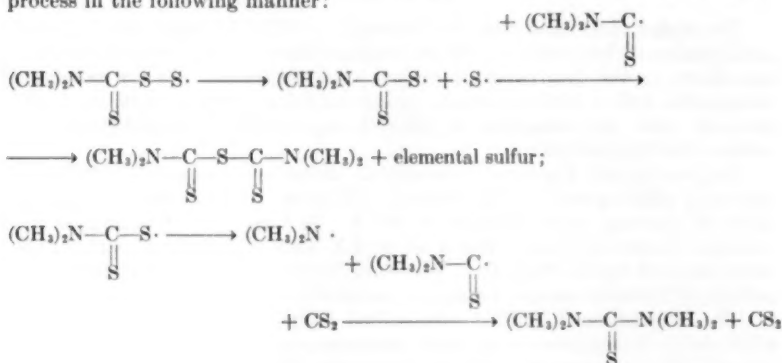
As is known, the interaction of TMTD with rubber is accompanied by formation of thermally stable, chemical crosslinks between molecules of rubber

chains. If only bimolecular reaction of TMTD with rubber were to occur, the addition product of TMTD to rubber and dithiocarbamic acid would form but crosslinking would not occur. Stable C—C bonds are formed, evidently, as a consequence of radical reactions. In direct confirmation of a radical mechanism there appear the results of examination of electron paramagnetic resonance spectra of a mixture of natural rubber with TMTD, heated in an atmosphere of argon and *in vacuo* at 140° and 180° (Figure 7)*.

As can be seen, the spectra have four peaks which upon cooling gradually disappear, and following heating reappear. During the process of heating at 180° for 50 minutes the height of the peaks abruptly decreased, i.e., the reaction of TMTD with rubber is completed.

Thermal degradation of TMTD radicals in the presence of rubber or other compounds with a labile hydrogen atom is less energetic than the attack of hydrogen atoms on the TMTD radicals or their reaction with the double bond. This is confirmed by the accumulation in the system of other products in the presence of such compounds. As already noted, tetramethylthiourea—characteristic of products of thermal degradation of TMTD—was not found by us in the interaction of TMTD with rubber, geraniol or isopropylbenzene.

The behavior of TMTD under vulcanization conditions suggests a peroxide-like action and the same for TMTD in initiation of polymerization[11]. The earlier noted maximum in the kinetic curve of combined sulfur of TMTD (distinguishing this process from other cases of vulcanization) may, evidently, explain which part of the thiuram grouping combines with rubber in the first stage, following which it is broken off in the form of carbon disulfide or dithiocarbamate remnants. Such a process is more likely for the fragment $(CH_3)_2N$—C—S—S·.

$$\begin{array}{c} \| \\ S \end{array}$$

This is confirmed by data on the combination of the sulfur of tetramethylthiuram monosulfide with rubber during heating in which case the maximum of the kinetic curve is absent.

The role of metal oxides in the process of rubber vulcanization by thiuram disulfide consists mainly in the binding of dithiocarbamic acid. As we noted earlier[1], products of its decomposition (carbon disulfide and dimethylamine) accelerate thermal oxidative degradation of the vulcanizate network. Therefore, when the binding of this acid in the form of a stable zinc salt does not occur under the conditions of vulcanization, there is clearly observed a pronounced appearance of reversion.

ACKNOWLEDGMENT

CONCLUSIONS

1. During vulcanization of rubber with tetramethylthiuram disulfide, sulfur and nitrogen in the form of radicals from TMTD combine with rubber. This is observed clearly as a pronounced maximum in the kinetic curves for sulfur combination during the first stage of vulcanization.

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* These experiments were carred out for us in the laboratory of S. E. Bresler in IVS AN USSR jointly with E. M. Saminskiĭ and E. H. Kazbekov. A more detailed analytical description of the spectra will follow in a future communication.

2. The presence of a maximum in the kinetic curve for the combination of TMTD sulfur with rubber is explained by decomposition of sulfur-containing radicals via combination with rubber with the formation of carbon disulfide.

3. The addition to rubber of unequal relative amounts of TMTD-derived sulfur and nitrogen allows the conclusion that under conditions of vulcanization there occur symmetrical and unsymmetrical decomposition of TMTD into the radicals

$$(CH_2)_2N-\underset{\underset{S}{\|}}{C}-S\cdot\,; \quad (CH_2)_2N-\underset{\underset{S}{\|}}{C}-S-S\cdot\,; \quad (CH_2)_2N-\underset{\underset{S}{\|}}{C}\cdot$$
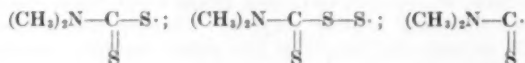
4. Reactions of these radicals with rubber lead to the formation of macro-radicals the interactions of which, one with another and with other molecules of rubber, lead to formation of the three dimensional network of the vulcanizate.

5. Dithiocarbamyl radicals accept hydrogen from α-methylenic groups of the rubber molecule to form dithiocarbamic acid which in the presence of zinc oxide forms the stable zinc dithiocarbamate. In this instance there is formed a dense three dimensional network and reversion is not manifested.

6. In mixtures without metal oxide and in mixtures with magnesium and calcium oxide, the dithiocarbamic acid which is formed on heating decomposes into dimethylamine and carbon disulfide. In this case reversion is observed owing to the acceleration of the thermal oxidative degradation of the vulcanizate network by these substances.

7. In mixtures of natural rubber containing lead and nickel oxide a three dimensional network is not formed on heating and from which carbon disulfide and dimethylamine are not evolved. Apparently, the metal dithiocarbamates formed in this case are bound to rubber.

8. The concentration of crosslinks in the vulcanizate increases with increasing content in the rubber of 1,4 monomer units. The amount of combined sulfur and the rate of accumulation of zinc dithiocarbamate are changed in inverse ratio.

9. During interaction of TMTD with geraniol and isopropylbenzene, just as with rubber, dithiocarbamic acid forms and subsequently decomposes to dimethylamine and carbon disulfide.

10. During heating of TMTD in the absence of substances containing an active hydrogen atom the decomposition proceeds with the formation of tetramethylthiuram monosulfide, carbon disulfide, tetramethylthiourea and sulfur.

SUMMARY

In the interaction of TMTD with rubber, sulfur and nitrogen from the TMTD add to the rubber, a maximum being exhibited on the rate curve for sulfur addition. At the same time dimethyldithiocarbamic acid is formed which, in mixtures containing zinc oxide, becomes bound in the form of Zn-DDC but which decomposes to carbon disulfide and dimethylamine in mixtures containing magnesium and calcium oxides and in the absence of metallic oxides. In the absence of oxides or in the presence of CaO or MgO a less dense three dimensional network is formed and reversion takes place which is accelerated by carbon disulfide and dimethylamine. The degree of crosslinking increases with increase in content of 1,4 structural units while the amount of combined sulfur and the rate of accumulation of zinc dithiocarbamate diminish.

Dithiocarbamic acid also forms in the interaction of TMTD with geraniol and isopropylbenzene. The thermal decomposition of TMTD to thiuram monosulfide, sulfur, tetramethylthiourea and carbon disulfide takes place in the absence of compounds with a labile hydrogen atom. The reaction proceeds through the stage of rupture of the S—S and C—S bonds of TMTD to form free radicals. The radical mechanism of the reaction is confirmed by electronic paramagnetic resonance specta.

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METAL OXIDES IN TETRAMETHYLTHIURAM DISULFIDE VULCANIZATION *

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Rubber is usually vulcanized with the aid of the so-called activators, metal oxides, zinc oxide being the one most often used. In vulcanization in the presence of MBT (mercaptobenzothiazole) or DPG (diphenylguanidine) as accelerators it was found[1] that vulcanization activators have almost no effect on the rate of addition of sulfur to rubber, but have a significant influence on the rate and degree of crosslinking of the rubber molecules. Special interest attaches to studies of the action of metal oxides in vulcanization with tetramethylthiuram disulfide (TMTD), as it is known from actual practice that in the absence of zinc oxide this accelerator does not bring about vulcanization.

Vulcanization with TMTD was studied on mixtures of natural rubber (extracted with cold acetone in a stream of nitrogen for 50 hours) and of synthetic isoprene rubber (SKI) masticated on microrolls, of the following compositions (in parts by weight).

Mixture No.	1	2	3	4	5	6	7	8
NR*	100	100	100	—	—	—	—	—
SKI	—	—	—	100	100	100	100	100
TMTD	2.5	2.5	2.5	4	4	4	4	4
Stearic acid	—	—	0.5	1	1	1	1	1
Zinc oxide	—	5	5	5	1	—	—	—
Magnesium oxide	—	—	—	—	—	0.5	—	—
Calcium hydroxide Ca(OH)$_2$·2H$_2$O	—	—	—	—	—	—	1.4	—

The vulcanization was effected in a press at 143° under a hydraulic pressure of 100 atmospheres. Under these conditions the interaction of TMTD with rubber is accompanied by the addition of sulfur and nitrogen to the rubber, probably in the form of radicals, together with other elements of TMTD. At the same time a portion of the TMTD is reduced to dithiocarbamic acid[2] which forms zinc dithiocarbamate in the presence of zinc oxide. As the result of these reactions chemical crosslinks are formed between the molecular chains of the rubber; the concentration of these crosslinks, determined from maximum swelling, can serve as a measure of the degree of vulcanization.

It is seen in Figure 1 that the accumulation of sulfur in the vulcanizates is represented by curves with pronounced maxima; this means that part of the added sulfur is split off from the rubber during subsequent heating. This removal of sulfur is the consequence of the formation of volatile products, as the ratio of the total sulfur in the rubber to the amount of sulfur introduced in the form of TMTD, decreases appreciably as heating proceeds (Figure 2). Metal oxides have little influence on the amount of sulfur added to the rubber. The
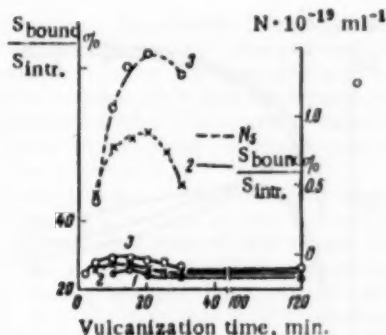
FIG. 1.—Variation of the amount of bound sulfur S_{bound}/S_{intr} from thiuram, and of the crosslink density N of the spatial network of vulcanizates of natural rubber with TMTD. *1*) Mixture No. 1; *2*) mixture No. 2; *3*) mixture No. 3.

influence of metal oxides on the amounts of volatile substances formed is more pronounced: in the presence of zinc oxide the loss of sulfur is slight, whereas in the absence of zinc oxide (and also in mixtures with magnesium oxide) up to 60% of the sulfur of the compounded (introduced) TMTD is liberated in the form of volatile compounds. Calcium hydroxide occupies an intermediate position. The influence of metal oxides on the formation of the spatial structure in the vulcanizates is very significant: in the absence of metal oxides a very sparse network is formed (the maximum swelling cannot be measured) in natural rubber mixtures at the vulcanization optimum, after 15–20 minutes of heating. Further heating leads to reversion—the vulcanizate again becomes completely soluble in hydrocarbons. Introduction of zinc oxide (5 parts) into the mixture favors a rapid increase of the crosslink content (at the vulcanization optimum in mixtures containing 5 parts ZnO $N_S = 0.9 \cdot 10^{19}$ ml^{-1}) and decreases reversion of vulcanization. In mixutres based on SKI containing ZnO practically no reversion occurs (Figure 3), but the effect is pronounced in mixtures containing MgO and Ca(OH)$_2$, and in mixtures without oxides. Therefore, as in the pre-
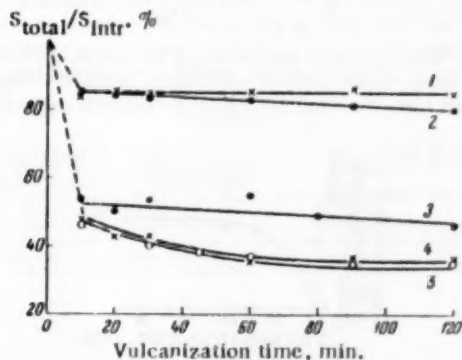
FIG. 2.—Variation of total thiuram sulfur in vulcanization of technical SKI rubber with TMTD. *1*) Mixture No. 4; *2*) mixture No. 5; *3*) mixture No. 7; *4*) mixture No. 6; *5*) mixture No. 8.
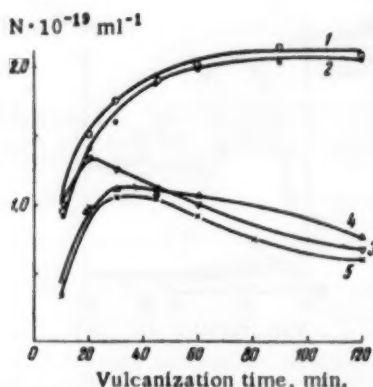
FIG. 3.—Variation of the density of the spatial network in the vulcanization of technical SKI with TMTD. *1*) Mixture No. 4; *2*) mixture No. 5; *3*) mixture No. 7; *4*) mixture No. 6; *5*) mixture No. 8.

viously investigated cases[1] of sulfur vulcanization in the presence of the mercapto thiazoles and DPG, in vulcanization with TMTD, metal oxides primarily influence the formation rate and concentration of chemical crosslinks. In the presence of zinc oxide (or zinc salts of fatty acids) dithiocarbamic acid is bound in the form of the zinc salt; its accumulation as vulcanization proceeds is shown graphically in Figure 4. In mixtures without zinc oxide, dithiocarbamic acid (or the rubber complex containing the dithiocarbamyl radical) decomposes with liberation of carbon disulfide, leading to a considerable decrease of the total and bound sulfur in the vulcanizate (Figure 2). The formation of carbon disulfide was detected by means of the qualitative reaction with ammonium molybdate[3]. The liberation of carbon disulfide is accompanied by formation of dimethylamine according to the equation
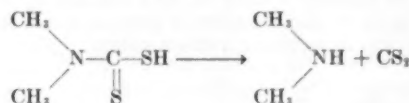
The formation of dimethylamine was detected by means of Nessler's reagent.

It is known that, under certain conditions, some secondary amines and similar compounds favor thermal and thermo-oxidative degradation of natural
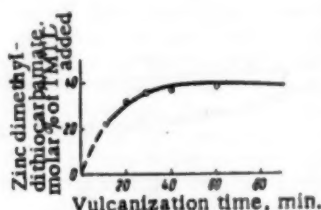
FIG. 4.—Kinetics of the formation of zinc dimethyldithiocarbamate in vulcanization of the following mixture: SKB (30% of 1, 2 structural units) 100 wt. parts; TMTD, 4 parts; ZnO, 5 parts; stearic acid, 1 part; phenyl-2-naphthylamine, 1 part.

rubber and its vulcanizates. For example, phenylhydrazine sharply lowers the viscosity of rubber solutions on heating[4]; phenyl-2-naphthylamine (in conjunction with xylyl mercaptan) favors the degradation of sodium butadiene vulcanizates[5]. Therefore it seems likely that the formation of the decomposition products of dithiocarbamic acid in the course of vulcanization also intensifies breakdown of the vulcanizate structure; in other words, it decreases the degree of crosslinking and leads to reversion.

Zinc dimethyldithiocarbamate is fairly stable under vulcanization conditions, and therefore binding of the acid by means of zinc oxide tends to increase the density of the vulcanization network and retards reversion. An indirect indication of this effect of zinc dimethyldithiocarbamate was obtained in our experiments on the viscosity changes of natural milled rubber on heating in an inert gas and in air at 143°. Zinc dimethyldithiocarbamate has no effect on the variation of the viscosity of rubber under these conditions; but in presence of butyric or benzoic acid, which themselves do not influence the viscosity of natural rubber, dimethyldithiocarbamate produces a considerable increase in the fall of viscosity on heating. The degradation in this case is probably associated with the formation (in an exchange reaction with the acids) and decomposition of dithiocarbamic acid.

Magnesium dithiocarbamate is not found in vulcanization in the presence of magnesium oxide; this leads to the conclusion that magnesium oxide does not combine with dithiocarbamic acid formed. Therefore in mixtures with magnesium oxide the same reversion occurs as in mixtures without oxides added as vulcanization activators.

In addition to the main action of zinc oxide in the vulcanization of rubber with TMTD, described in this paper, some of the processes described previously[1] may also take place.

The direction of the reactions between TMTD and rubber depends to a considerable extent on the type of rubber. It was found that in the vulcanization of butadiene rubbers the amount of zinc dimethyldithiocarbamate formed and the amount of bound sulfur increase with increasing relative contents of the 1, 2 structure in the polymer. This means that the mobile hydrogen at the tertiary carbon atom in the molecular chain takes part in the reduction of TMTD. At the same time the degree of crosslinking, as was shown earlier for other types of vulcanization[6], increases with increasing contents of the 1, 4 structure in the polymer. Therefore the spatial structure is formed mainly from the principal chains in the rubber. The mechanism of the presumed reactions will be discussed in a future communication.

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SYNTHESIS OF POLYSULFIDES CONTAINING POLAR LINKAGES *

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Polysulfide polymers are usually prepared from dihalogen compounds and sodium polysulfide and are used as synthetic rubbers. Also, polyamides or polyurethanes, such as Nylon 66, Perlon U (Igamid U) or Vulcollan, are used because of certain good properties. Therefore, if new polysulfide polymers could be produced when sodium polysulfide reacts with a dihalide having a polar linkage such as an amide group, we might expect excellent properties in the new materials because they might contain urethane, urea or amide linkages.

We now show that dichloro compounds, which contain urethane linkages, can be prepared by the reaction between a chlorohydrin (ethylene chlorohydrin or 4-chlorobutanol-1) and polymethylene diisocyanate (where $n = 3$, 4, 6 and 8 in $(CH_2)_n$).

$$2\,Cl—(CH_2)_mOH + OCN\,(CH_2)_nNCO \longrightarrow$$
$$Cl—(CH_2)_m\underset{\underset{O}{\|}}{O}C—NH—(CH_2)_n—NH\underset{\underset{O}{\|}}{C}—O(CH_2)_mCl$$
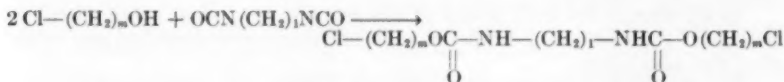
The reactions were carried out in solution in benzene or ether at room temperature or under heating. The products were recrystallized from benzene solution.

The dichloro compounds, which have urea linkages, were prepared by the following two methods:

(1) Addition reaction between chloroethylamine and polymethylene-diisocyanate (where $n = 4$, 8 in $(CH_2)_n$).

$$Cl—CH_2CH_2NH_2 + OCN\,(CH_2)_nNCO \longrightarrow$$
$$Cl—CH_2CH_2NHCONH\,(CH_2)_nNHCONHCH_2CH_2Cl$$

(2) Ring-opening and addition reaction of polymethylene-bis(ethylene urea) in an ethereal solution.

$$\underset{CH_2}{\overset{CH_2}{\Big|}}{>}NCONH(CH_2)_6NHCON{<}\underset{CH_2}{\overset{CH_2}{\Big|}} + 2\,HCl \longrightarrow$$
$$ClCH_2CH_2NHCONH\,(CH_2)_6NHCONHCH_2CH_2Cl$$
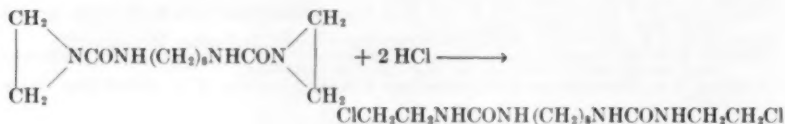
By method (2), we were able to get dichloro compounds in good yields (60%).

The dichloro compounds, having amide linkages, were prepared from
ω-chloroacyl chlorides (chloroacetyl chloride and β-chloropropionyl chloride)
and polymethylene diamine (where $n = 2, 4, 6$ in $(CH_2)_n$).

$$2 Cl(CH_2)_mCOCl + H_2N(CH_2)_nNH_2 \longrightarrow$$
$$Cl(CH_2)_mCONH(CH_2)_nNHCO(CH_2)_mCl$$

The dichloro compounds, which have urethane linkages, such as $ClCH_2CH_2$-
$OOCNH(CH_2)_4NHCOOCH_2CH_2Cl$, for instance, were treated with a boiling
sodium tetrasulfide solution or methanol solution for 8–10 hours. The yield
of condensation product was about 41–62%. Some attempt must be made to
prevent hydrolysis, as we detected the odor of tetramethylenediamine.

$$ClCH_2CH_2OOCHN(CH_2)_4NHCOOCH_2CH_2Cl + Na_2S_4 \longrightarrow$$
$$(-CH_2CH_2OOCNH(CH_2)_4NHCOOCH_2CH_2S_4-)_n + 2 NaCl$$

I

The polyurethane polysulfide obtained in this case was a transparent and
elastic compound and the other polyurethane polysufide (—CH_2CH_2OOCNH-
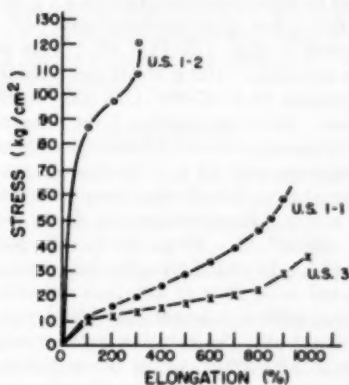
FIG. 1.

$(CH_2)_6NHCOOCH_2CH_2S_4-)_n$ was more or less rigid and had the property of
melt spinability. The compound, $(-CH_2CH_2OOCNH(CH_2)_2NHCOOCH_2-$
$CH_2S_4-)_n$ (II), has a low softening point and low elasticity; also $(-CH_2CH_2-$
$CH_2CH_2OOCNH(CH_2)_4NHCOOCH_2CH_2CH_2CH_2S_4-)_n$ has a low softening
point and high plasticity.

The polyurethane polysulfides were masticated with zinc oxide and pressed
into sheets. I and II could be made into sheets; elongation, strength and re-
sistance to chemicals were examined. These properties were excellent as we
had anticipated. The stress-strain properties are shown in Fig. 1.

Dichloro compounds, which have urea linkages, such as $ClCH_2CH_2NH$-
$CONH(CH_2)_4NHCONHCH_2CH_2Cl$ (III) and $ClCH_2CH_2NHCONH(CH_2)_6$-
$NHCONHCH_2CH_2Cl$, were treated with sodium tetrasulfide and gave rise to
polyurea polysulfides. These could not be masticated and (—CH_2CH_2NH-

CONH(CH$_2$)$_8$NHCONHCH$_2$CH$_2$S$_4$—)$_n$ was a product having spinability but the fibers were fragile.

$$VII + Na_2S_4 \longrightarrow (—CH_2CH_2NHCONH(CH_2)_4CHCONHCH_2CH_2S_4—)_n$$
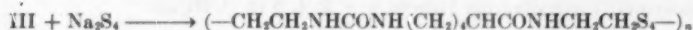
The polycondensation products, from the reaction between dichloro compounds containing amide linkages and sodium tetrasulfide, have no elasticity but rather spinability.

$$ClCH_2CH_2CONH(CH_2)_6NHCOCH_2CH_2Cl + Na_2S_4 \longrightarrow$$
$$(—CH_2CH_2CONH(CH_2)_6NHCOCH_2CH_2S_4—)_n$$
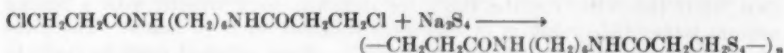
Considering the hydrogen bonding of urea and amide linkages in these polyurea polysulfide and polyamide polysulfides, we can expect good elasticity in the derivatives which have more methylene linkages[1].

EXPERIMENTAL

SYNTHESIS OF POLY(URETHANESULFIDES)

Tetramethylene-bis(chloroethylurethane).—A 2.8 g portion of tetramethylene diisocyanate was added to an ethereal solution of 3.2 g of ethylene chlorohydrin in a sealed bottle. After a few days crystals came out; recrystallization from methanol gave a product of m.p. 113–114° C[1]. This reaction is more easily carried out in benzene solution. 100 g of ethylene chlorohydrin and 85.4 g of tetramethylene diisocyanate (b.p. 87–88° C/4 mm) were dissolved in benzene and boiled for six hours. Recrystallization from benzene gave white crystals, m.p. 113–114° C. *Tetramethylene-bis(chlorobutylurethane).*—A 7 g portion of tetramethylene diisocyanate and 12 g of 4-chlorobutanol (b.p. 75–80° C/14 mm), which was prepared from tetrahydrofuran, was dissolved in benzene and then heated for two hours. Recrystallization from benzene gave 10.5 g of white crystals, m.p. 89–90° C. Yield—53%. *Trimethylene-bis(chloroethylurethane)* (Cl$_2$C$_9$H$_{16}$N$_2$O$_4$).—Distilled trimethylene diisocyanate (b.p. 97° C/21 mm) (15 g) were treated with 20 g of ethylene chlorohydrin in a flask fitted with a Liebig condenser with a calcium chloride drying tube. After a five-hour reaction on a warm bath, the solution gave crystals. Recrystallization from benzene gave m.p. 89.5–90.5° C, in quantitative yield. Analysis: N, 10.19% found; 9.79% calcd. *Octamethylene-bis(chloroethylurethane).*—9.8 g of octamethylene diisocyanate (b.p. 128–132° C/3.5 mm) and 8.2 g of ethylene chlorohydrin were dissolved in benzene and then heated for three hours. After standing overnight, crystals were obtained which, on recrystallizing from methanol, gave white crystals, m.p. 108–109° C. Yield—90%. N, 7.95% found; 7.84% calcd.

Polycondensation of tetramethylene-bis(chloroethylurethane) and sodium tetrasulfide.—(a) *Solution method.*—Sodium sulfide (24 g) and 9.6 g of sulfur were dissolved into 200 cc of water under stirring and then heated. 400 cc of water and 15 g of chloroethylurethane were added to the solution and allowed to react for ten hours. 12 g of product was obtained. Yield—62.8%, softening point, 103–105° C. N, 7.26% found; 7.82% calcd. The sample obtained here is called US1-1.

(b) *Solution method with magnesium hydroxide as dispersing agent.*—Magnesium hydroxide was added as in the previous experiment. This magnesium hydroxide was prepared from 40 g of MgCl$_2$·4H$_2$O and 20 g of NaOH. After

ten hours reaction, magnesium hydroxide was washed off by adding dilute hydrochloric acid.   The polymer obtained was dried after washing with hot water.   Yield—27%.   This sample is called US1-2.

(c) *Methanol solution method.*—Sodium sulfide and sulfur were added to methanol and sodium tetrasulfide was prepared.   The methanol solution of *bis*-chloro compound was added and allowed to react for seven hours with boiling.   Greenish-gray rubbery polymer was obtained.   Yield—41%.   The elongation of the crude product was 300%.

Polycondensation of tetramethylene-bis(chlorobutylurethane) and sodium tetrasulfide.—One hundred cc of the solution of sodium tetrasulfide (prepared from 6.7 g of $Na_2S \cdot 9H_2O$ and 2.7 g of sulfur) was added to a mixture of 5 g of *bis*-chlorourethane and 400 cc of water and then treated for ten hours under boiling. A greenish-yellow polymer was obtained quantitatively.   Softening point was 70° C and spinability was excellent.

Polycondensation of trimethylene-bis(chloroethylurethane) and sodium tetrasulfide.—Two hundred cc of the solution of sodium tetrasulfide prepared from 25 g of sodium sulfide and 10 g of sulfur was treated with the dichloro compound for ten hours.   The polymer was greenish-yellow, elastic; softening point, 109–110° C.   Yield—74%.   This sample is called US-3.

Polycondensation of octamethylene-bis(chloroethylurethane) and sodium tetrasulfide.—*bis*-Chlorourethane (4 g) was added to the solution of sodium tetrasulfide prepared from 5.4 g of sodium sulfide and 2.2 g of sulfur and treated for one hour at 100° C.   A brown polymer was obtained.   Yield—93%.   Softening point 68–70° C.   It was spinable.

PROPERTIES

The properties of US1-1, US1-2 and US-3 were tested.   The US1-1 was masticated on a mill at 100–105° C, and zinc oxide (about 10% by weight) was added, blended for ten minutes and then vulcanized at a steam pressure of 50 kg/cm² for 30 minutes at 110° C.   A dark greenish elastic sheet was obtained. Dumbbell specimens were tested on a stress-strain machine with results shown in Figure 1.

The US1-2 was masticated on rolls for ten minutes at 80–90° C.   Zinc oxide was added (about 10% by weight) and masticated for 20 minutes.   Fifty per cent by weight of carbon black (on the rubber) was added, the mix masticated, and then vulcanized at 110° C for 30 minutes under a pressure of 50 kg/cm². Test sheets were examined as above.

The US-3 was treated as US1-1.   Mastication was carried out near the temperature of the softening point.   Vulcanization was carried out at 100–120° C under 22.5 kg/cm² for four minutes and then 50 kg/cm² for 36 minutes.

Resistance to organic chemicals for each sample was tested.   After immersing each sample for 50 hours, the increase or decrease of weight was measured with results shown in Table I.

TABLE I

Test chemicals	US1-1	US1-2	US-3
Ligroin	+0.04%	+0.05	+0.61
Benzene	+0.34	+0.40	+0.24
Toluene	+0.07	+0.06	+0.49
Dil. HCl	−0.08	0.0	+0.41
Dil. NaOH	+0.42	+0.22	+0.64
Water	+0.19	+0.16	+0.23

POLYUREA POLYSULFIDES

Synthesis of dichloro compounds having urea linkages.—Tetramethylene bis (chloroethylurea).—Chloroethylamine hydrochloride (m.p. 132–133° C) was prepared from the reaction of ethanolamine and thionyl chloride. 12 g of this salt and 5.7 g of tetramethylene diisocyanate were added to 100 cc of ether in a flask, under stirring and cooling; 16.5 g anhydrous sodium carbonate, was added to the solution in three portions during two and a half hours. The reaction was carried out until the ethereal solution became alkaline (about 4 hours). After filtration, *bis*-chloro compound was extracted from the precipitate with ether (200 cc). White crystals were obtained after cooling of the ethereal solution. Recrystallization from methanol several times gave white crystals, m.p. 144–146° C; yield—41%. N, 18.32% found; 18.73% calcd.

Octamethylene bis(chloroethylurea).—(a) *From chloroethylamine and octamethylene diisocyanate.*—Chloroethylamine hydrochloride (11.6 g) and 9.8 g of octamethylene diisocyanate were treated in ethereal solution. 8.2 g of sodium carbonate was added in three portions. Seven hours were required for reaction. *bis*-Chloro compound was extracted from the precipitate with ether. Recrystallization from methanol gave white crystals, m.p. 147–148° C. 2 g of product was obtained. Yield—11.3%. N, 15.15% found; 15.75% calcd.

(b) *From octamethylene bis(ethyleneurea) and hydrogen chloride.*—An alcoholic solution of octamethylene *bis*-ethyleneurea containing 1 g by weight was added to an alcoholic solution which contains 2 g of hydrogen chloride gas in a 20 cc of alcohol. After refluxing for three hours, the solution was concentrated under vacuum. A white crystalline material was obtained from the viscous solution on adding water; it was filtered and then recrystallized from methanol using decolorizing carbon. M.p. 147–148° C, 0.7 g. Yield—60%.

Synthesis of polysulfide.—Polycondensation of tetramethylene bis(chloroethylurea) and sodium tetrasulfide.—(a) *Solution Method.*—Sulfur (1.3 g) was added to a solution composed of 3.2 g of sodium sulfide in 23 cc solution. 50 cc. of water was added and then the solution was heated to 100° C. Dichloroethylurea (2 g) was added and the mixture allowed to react for 11 hours. The precipitate was filtered off and washed with hot water. After washing with acetone, the product obtained had 183° C for a softening point and decomposed at 224° C. Yellow powder.

(b) *Methanol solution method—bis*-Chloroethylurea was added to a solution of sodium tetrasulfide in methanol. The reaction was carried out for 10 hours. The precipitate was treated as above. Softening point was 180° C and the product decomposed at 227° C. Yellow powder, 1.2 g. Yield—50%. N, 16.15% found; 15.78% calcd. This product could not be made into a sheet.

Polycondensation of octamethylene bis(chloroethylurea) and sodium tetrasulfide. —Two g of dichloro compound was added to a sodium tetrasulfide solution prepared from 2.7 g of sodium sulfide and 1.1 g sulfur and 80 cc of water. Reaction was carried out for 13 hours. The precipitate was filtered and washed with hot water and then washed twice with acetone. Softening point was 173° C. Brown powder. Yield—50%. Decomposed at 191° C. N, 14.45% found; 13.59% calcd. This powder had excellent spinability but did not give a sheet by mastication.

POLYAMIDEPOLYSULFIDE

Synthesis of dichloro compounds having amide linkages.—Tetramethylene-bis (chloroacetamide) is obtained from the reaction of chloracetyl chloride and tetra-

methylene diamine in a chloroform solution in the presence of tetramethylene diamine and potassium carbonate or triethylamine under cooling. Chloroacetyl chloride was obtained from mono chloroacetic acid with thionyl chloride and distilled at 105–105.5° C. In the case of using the diamine itself as the acid acceptor, the yield was 75–85%; in the case of potassium carbonate—38%, and triethylamine—43%. Tetramethylene dichloroacetamide was recrystallized from water. M.p. 134–135° C. Yield—80.2%. N, 11.21% found; 11.62% calcd.

Hexamethylene-bis(chloroacetamide).—Chloroacetyl chloride (5 g) in 40 cc of chloroform was added to a 30 cc of solution of chloroform which contained 5.1 g of hexamethylene diamine. White crystals. M.p. 132.5° C, 4.4 g., 74.5%. N, 10.41% found; 10.41% calcd.

Ethylene-bis(β-chloropropionamide).—β-Chloropropionyl chloride was prepared from β-propiolactone with thionyl chloride[2]. B.P. 51° C/31 mm. 7.6 g of β-chloropropionyl chloride in 20 cc of chloroform was dropped into 20 cc of a solution of chloroform containing 3.6 g of ethylenediamine. Recrystallization from water gave 11.6 g, m.p. 189.5–190° C. Yield—80%. N, 11.59% found; 11.62% calcd.

Tetramethylene-bis(β-chloropropionamide).—It is prepared from 7.62 g of β-chloropropionyl chloride and 5.28 g of tetramethylene diamine. M.p. 164° C, 6.8 g. Yield—85%. N, 10.46% found; 10.41% calcd.

Hexamethylene-bis(β-chloropropionamide).—β-chloropropionyl chloride (6.35 g) and 5.8 g of hexamethylene diamine were reacted in a chloroform solution. M.p. 149–150° C, 12.5 g. Yield—84%. N, 9.08% found; 9.43% calcd.

Polycondensation of tetramethylene-bis(chloroacetamide) and sodium tetrasulfide.—Two and five tenths g of dichloro compound was added to an aqueous solution containing 4.5 g of sodium tetrasulfide at 95° C under stirring. Reaction was carried out at 100° C for 8 hours. The product was washed by hot water and then washed with acetone. 3.1 g quantitative yield. Softening point, 140–150° C, decomposed above 200° C. N, 8.05% found; 9.39% calcd. S, 40.43% found; 43.03% calcd. This product has spinability from the melt but the fiber was fragile.

Polycondensation of hexamethylene-bis(chloroacetamide) and sodium tetrasulfide.—Two and two tenths g of dichloro compound and 2.5 times the theoretical weight of sodium tetrasulfide were treated at 95° C for 5 hours, and then 100° C for 2 hours. Product was obtained quantitatively; softening point was 110° C. This product has spinability from the melt. N, 7.45% found; 8.59% calcd. S, 32.72% found; 39.26% calcd.

Polycondensation of ethylene-bis(β-chloropropionamide) and sodium tetrasulfide.—Two and four tenths g of dichloro compound and 2.5 times the theoretical weight of sodium tetrasulfide were treated for 8 hours. White-yellow product was obtained and its softening point was 170–180° C. N, 8.95% found; 9.30% calcd.

Polycondensation of tetramethylene-bis(β-chloropropionamide) and sodium tetrasulfide.—Two and seven tenths g of dichloro compound was treated with 2.5 times the theoretical weight of sodium tetrasulfide at 100° C for 8 hours. White-yellow crystalline material was obtained, m.p. 180° C. Yield—90%. Spinable. N, 7.73% found; 8.95% calcd.

Hexamethylene-bis(β-chloropropionamide)and sodium tetrasulfide.—Three g of dichloro compound was treated with 1.5 times the theoretical weight of

sodium tetrasulfide at 90° C for 8 hours.   Gray powder was obtained.   Soften-
ing point was 180° C.   Yield—90%.   Spinable.   N, 7.95% found; 7.91%
calcd.

ACKNOWLEDGMENT

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STRESS RELAXATION DURING THE THERMAL OXIDATION OF VULCANIZED NATURAL RUBBER *

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The photoinitiated oxidative aging of peroxide vulcanized natural rubber (which contains only carbon-carbon cross-links) was found[1] by stress relaxation measurements[2] to be autocatalytic and to be sensitive to the presence of free radical retarders and catalysts. Similar behavior would be expected in thermal aging. However, earlier work in these laboratories[3] indicated that the thermal aging of peroxide vulcanizates was not autocatalytic. Because of this discrepancy the stress relaxation of peroxide vulcanizates at elevated temperatures has now been reinvestigated and the study has been extended to include also the aging of the other types of networks which are produced on vulcanization by tetramethylthiuram disulfide in the absence of sulfur, by sulfenamide-sulfur, and by sulfur alone.

EXPERIMENTAL

Materials.—Samples of the various grades of rubber employed, all continuously extracted for 24 hr with hot acetone and dried *in vacuo* before use, gave the following analyses: deproteinized (DP) crepe (supplied by the Indonesian Rubber Research Organization) N, 0.20%, O, 0.65%, ash $\geqslant$ 0.01%; "Highly Purified" (HP) rubber (U.S. Rubber Co.) N, 0.05%, O, 0.1%, ash 0.09%; ribbed smoked sheet (RSS1) N, 0.45%, O, 0.7%, ash 0.21%.

α- and β-naphthol were A.R. materials and were not further purified. Antioxidant 425 (2,2'-methylene-*bis*[4-ethyl-6-*tert*-butylphenol]) was a commercial product of the American Cyanamid Co. Benzoyl peroxide was purified by precipitation from chloroform solution with acetone.

Preparation of vulcanizates.—Vulcanizing ingredients were incorporated on a small two roll mill and crosslinking was effected by heating in a $10 \times 10 \times 0.02$ cm mold at 140° C under a pressure of 1 ton/sq in. The recipes employed, in parts by weight per hundred parts of rubber (phr), and the cure times were: (i) peroxide vulcanizates: dicumyl peroxide 2; 35 min; (ii) tetramethylthiuram disulfide (TMTD) vulcanizates: TMTD 4, zinc oxide 5; 120 min; (iii) sulfenamide-sulfur vulcanizates: N-cyclohexyl-2-benzthiazolyl sulfenamide (Santocure of Monsanto Ltd.) 0.7, sulfur 2.5, zinc oxide 5, stearic acid 1; 25 min; (iv) unaccelerated sulfur vulcanizates: sulfur 10; 270 min. The vulcanized sheets were continuously extracted with hot acetone for 24 hr, dried and stored *in vacuo*.

The heating period for the TMTD vulcanizate was considerably longer than the usual 40 min since this type of vulcanizate when not fully crosslinked contains a nonextractable intermediate compound which breaks down during aging producing the powerful antioxidant, zinc dimethyldithiocarbamate[4].

Incorporation of antioxidants and initiators.—When required, additives were incorporated into the extracted vulcanizates by swelling the strips overnight in ethyl acetate solutions and drying off the solvent at 10^{-2} mm. Since ethyl acetate solutions swelled the vulcanizates to approximately twice their original volume, the concentrations of additives in the rubber were approximately the same as those in the swelling solutions. The present investigation did not necessitate accurate knowledge of the concentration of these materials in the rubber and the concentrations quoted subsequently are those of the swelling solutions.

Measurement of stress relaxation.—The apparatus employed for measuring the decay in tension in a strip held at constant extended length has been described previously[1, 5] An initial period of 30 min at reaction temperature was

HP rubber.   DP crepe

● peroxide cure at 80°   ○ peroxide cure at 90°
◐ peroxide cure at 100°   ◑ TMTD cure at 80°
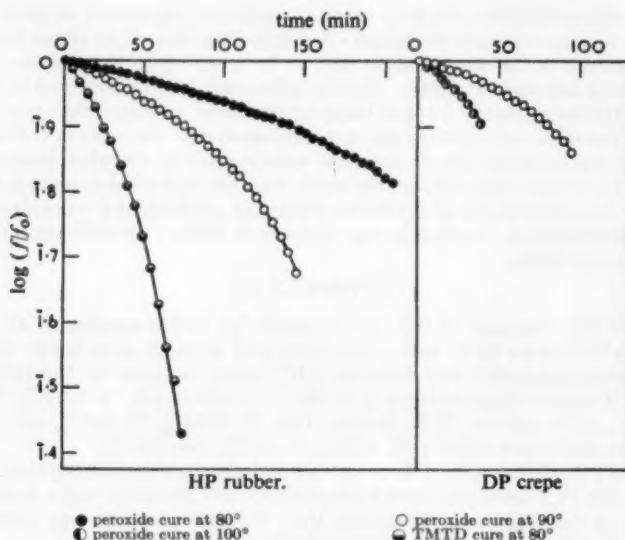
Fig. 1.—Stress relaxation in air of dicumyl peroxide and TMTD vulcanizates of DP crepe and HP rubber at various temperatures.

normally allowed for attainment of thermal equilibrium before readings were taken.

RESULTS

Sulfurless vulcanizates.—The results of stress relaxation measurements on peroxide and TMTD vulcanizates of HP rubber and on a peroxide vulcanizate of DP rubber during thermal aging in air are given in Figure 1 as graphs of log stress against time. The degradative reaction is clearly autocatalytic, none of the curves showing any linear portion.

The effects of 1- and 2-naphthol, of Antioxidant 425 and of benzoyl peroxide on the stress relaxation in air at 80° C of both peroxide and TMTD vulcanizates of HP rubber are shown in Figure 2. The additives were introduced from 0.2% and 1.0% solutions as indicated. Phenolic antioxidants, even at the lower concentration, markedly reduced the rate of degradation. Benzoyl
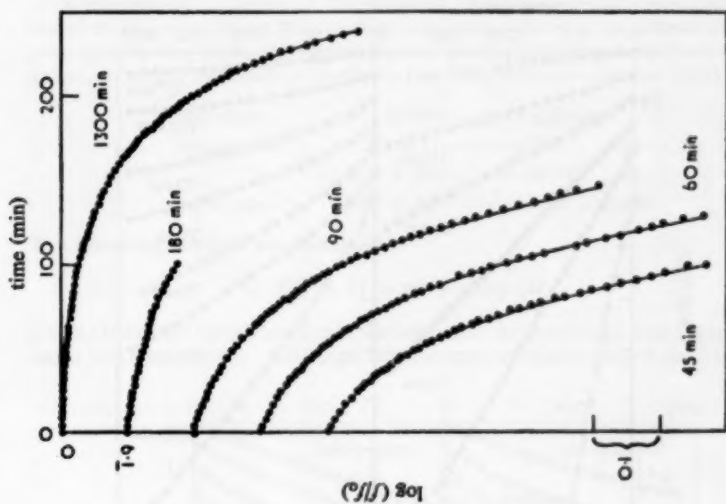
Fig. 3.—Stress relaxation at 80° C in air of dicumyl peroxide vulcanisates of HP rubber after preheating in vacuo for various times.
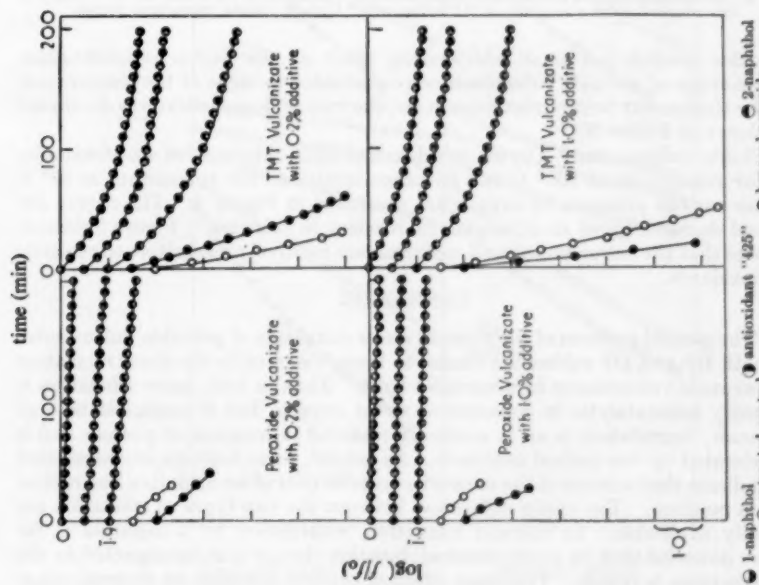
Fig. 2.—Stress relaxation at 80° C in air of dicumyl peroxide and TMTD vulcanisates of HP rubber containing phenolic antioxidants or benzoyl peroxide. TMT = TMTD.
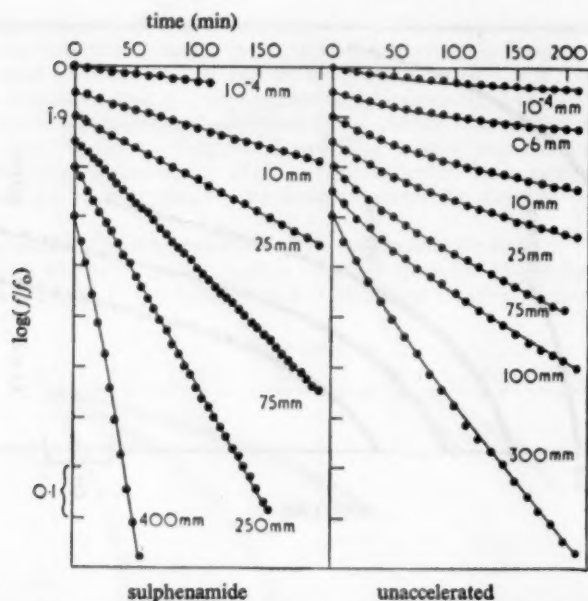
FIG. 4.—Stress relaxation of a sulfenamide-accelerated sulfur vulcanizate of HP rubber at 100° C and of an unaccelerated sulfur vulcanizate of HP rubber at 80° C under various pressures of oxygen.

peroxide exhibited a small accelerating effect at the higher concentration. When strips of peroxide vulcanizate were preheated *in vacuo* at the temperature of the thermostat before relaxation in air, the rate of degradation was decreased as shown in Figure 3.

Sulfur vulcanizates.—The stress relaxation data obtained for a sulfenamide-sulfur vulcanizate at 100° C and an unaccelerated sulfur vulcanizate at 80° C under various pressures of oxygen are presented in Figure 4. The curves obtained do not suggest an autocatalytic reaction in this case. Figure 5 demonstrates that the sulfur-vulcanized materials are relatively insensitive to phenolic antioxidants.

DISCUSSION

The general features of the thermal stress relaxation of peroxide vulcanizates of both HP and DP rubber are similar to those observed in the stress relaxation of peroxide vulcanizates in ultraviolet light. Thus in both cases relaxation is strongly autocatalytic in presence of air or oxygen, but is negligible in high vacuum; degradation in air is markedly retarded in presence of phenols and is accelerated by free radical initiators. As before[1], these features are considered to indicate that scission of the network occurs as part of an oxidative free radical chain reaction. The minor differences between the two types of relaxation are readily explicable. In thermal relaxation, retardation by 2-naphthol is far more powerful than in photochemical, but this change is to be expected as the temperature is raised. The lesser effect of benzoyl peroxide on thermal relaxation is probably due to a slower rate of breakdown at 80° C than under the 365 mµ irradiation used.

A theoretical analysis of the kinetics of photochemical degradation was based on the assumption that scission may occur either as an alternative to the propagation step or to the initiation step in the following autoxidation mechanism, in which termination is effected by adventitious retarder (AH):

initiation	$ROOH \longrightarrow$ radicals	(1)
propagation	$R \cdot + O_2 \longrightarrow RO_2 \cdot$	(2)
	$RO_2 \cdot + RH \longrightarrow ROOH + R \cdot$	(3)
termination	$RO_2 + AH \longrightarrow$ inert products	(4)
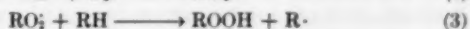
The following relation was obtained:

$$f_0/f = (1 - a) + a \exp (kt) \tag{1}$$

f_0 and f being the initial tension in the strip and the tension at time t respectively and a and k constants. Although this theoretical relationship is doubtless only
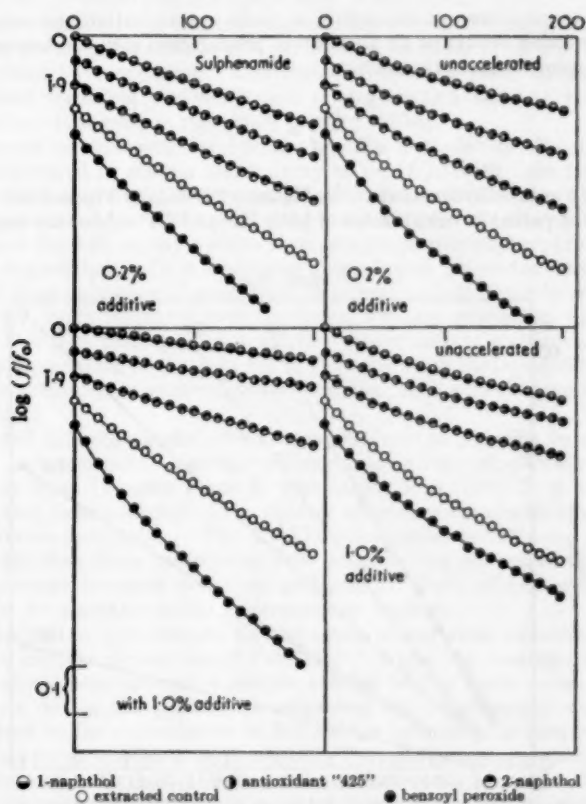
FIG. 5.—Stress relaxation of a sulfenamide-accelerated sulfur vulcanizate of smoked sheet in air at 100° C and of an unaccelerated sulfur vulcanizate of HP rubber in air at 80° C in presence of phenolic antioxidants or of benzoyl peroxide.

approximately correct since it is based on the prediction of the simple elasticity theory that the tension is proportional to the number of network chains, it was satisfied with good accuracy by the experimental data, further confirming the mechanism suggested by the qualitative features of the relaxation.

In spite of the qualitative similarity of the thermal and photochemical stress-time data, the former could not be represented satisfactorily by Eqn. (1). However, it is well-known[6] that in thermal autoxidations of olefins the initiation step is commonly second order in hydroperoxide so that Eqn. (1) being based on a first order initiation could no longer be expected to apply. With an initiating step

$$2 \text{ ROOH} \longrightarrow \text{radicals} \tag{1a}$$

and a termination reaction first order in radicals as (4) the overall rate of formation of hydroperoxide is

$$d[\text{ROOH}]/dt = k[\text{ROOH}]^2 \tag{2}$$

k being a pseudo constant depending on olefin concentration and oxygen pressure. If scission occurs as an alternative propagation step the treatment previously employed[1] gives the relation

$$\frac{f}{f_0 - f} = \frac{a}{t} - b \tag{3}$$

with a and b as pseudo constants. In Figure 6 the data of Figure 1 for the stress relaxation of peroxide vulcanizates of both HP and DP rubber are replotted as
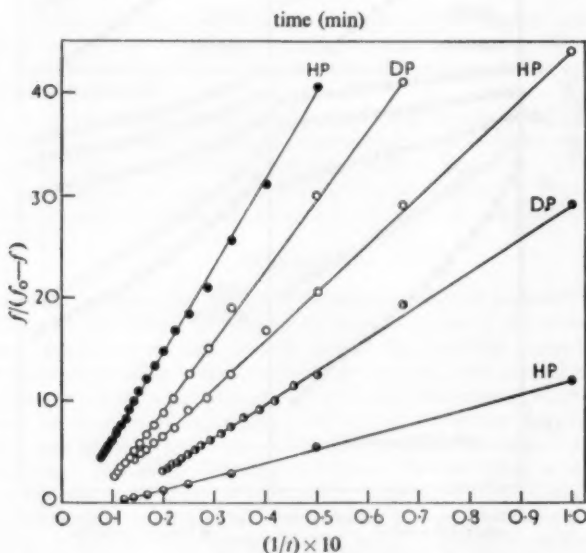
FIG. 6.—Data of Figure 1 replotted as $f(f_0 - f)$ against $1/t \times 10$ in accordance with theoretical relationship (3).

$f/(f_0 - f)$ against $1/t$ as suggested by Eqn. (3); good straight lines result in all cases.

If scission of the polymer chains is involved in the initiation reaction (1a) an equation of the same form as (3) is again obtained and such a mechanism would provide an equally satisfactory explanation for the present results. It was similarly shown in the photochemical case that the experimental results were equally well fitted by either of the two corresponding treatments. Scission occurring as an initiation step would not, of course, involve the same reaction in the two cases as the thermal and photochemical initiation reactions differ.

The effect of preheating the strips *in vacuo* before measurements of stress relaxation in air (Figure 3) accords with the degradation mechanism proposed above, since the gradual destruction of chain-initiating hydroperoxide during preheating would result in an initial relaxation rate which decreased with preheating time. After lengthy preheating the stress relaxation data did not so accurately fit the theoretical relationship (3). However, at low concentrations hydroperoxide decomposition is first order rather than second order[3], which would reduce the initial acceleration of rate, as observed.

Since the completion of this investigation the results of a comparable study by Ore[7] on the stress relaxation of a peroxide vulcanizate of carefully purified natural rubber have appeared. Conclusions similar to those outlined above were reached regarding the mechanism of degradation and the presence of natural antioxidant even in rigorously purified rubber.

The earlier experimental data[3] on the thermal degradation of peroxide vulcanizates appeared to show a linear decay of log (f/f_0) with time rather than autocatalytic degradation. On re-examination, the earlier data have proved to be inadequate for a clear distinction to be made between the alternative mechanisms, since the 0.01 cm thick strips then used frequently ruptured in the early stages of degradation. In a few cases, degradation proceeded farther than usual, and these data showed an increase in relaxation rate in the later stages of degradation. Such increases were, however, wrongly attributed to physical effects such as slow tearing prior to rupture rather than to a chemical process. This misinterpretation of the data led to the conclusion that oxidative scission of peroxide vulcanizates occurred at the crosslink; such a mechanism must now be discarded.

Extracted thiuram vulcanizates behave similarly to peroxide vulcanizates; thus they are sensitive to phenolic antioxidants and the stress-time data obtained from them (Figures 1 and 6) also satisfy Eqn. (3). It is concluded, therefore, that these also degrade by random scission of the chains as part of an olefin oxidation mechanism. The TMTD vulcanizates investigated degraded more rapidly than those crosslinked with peroxide and showed an even more marked decrease in stress decay on preheating. Both effects could be accounted for by a greater initial hydroperoxide content.

The mechanism put forward for the aging of *sulfurless* vulcanizates is in accordance with the conclusions of Tobolsky[2, 9, 10] who has, however, suggested that *all* vulcanizates undergo oxidative scission of the main chain. Experiments made during the present investigations using sulfenamide-sulfur and unaccelerated sulfur vulcanizates of HP rubber bear on this question of the generality of the autoxidative mechanism. The results obtained showed many notable contrasts with those obtained using sulfurless vulcanizates. Thus, the relaxation curves (Figure 4) were of quite a different shape, and showed a steady increase in rate with oxygen pressure even at high pressures, which is not in line with olefin oxidation. The effect of phenolic antioxidants (Figure 5) was much

less marked; while 0.2% of antioxidant reduced the stress relaxation of a per-
oxide vulcanizate manyfold, 1% only reduced the relaxation rate of a sulfen-
amide-accelerated vulcanizate by a factor of about 3.   An even more marked
contrast arises in the presence of metal dialkyldithiocarbamates which were
recently shown to afford excellent protection to sulfurless vulcanizates at 100° C
at a concentration of 0.2%, but to be ineffective in sulfenamide-accelerated
vulcanizates[4].   A further distinction between the classes of vulcanizate lies in
the crosslinking reaction accompanying degradation of sulfur vulcanizates,
which, as Figure 8 shows, almost balanced the degradation.   This reaction
cannot be attributed to continued vulcanization since the free sulfur has been
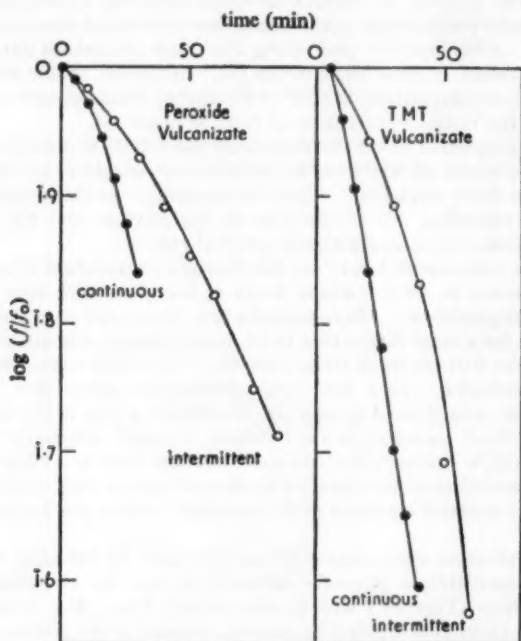
Fig. 7.—Intermittent and continuous stress relaxation of extracted dicumyl peroxide and
TMTD vulcanizates of HP rubber in air at 80° C.   TMT = TMTD.

reduced to 0.5% by extraction.   With sulfurless vulcanizates this crosslinking
was much less relative to the degradation (Figure 7).
      These differences indicate that the mechanism of scission of sulfur vulcani-
zates is considerably different from that of sulfurless vulcanizates and probably
involves crosslinks as suggested by Berry and Watson[3].   It is difficult to
reconcile these distinctions with Tobolsky's view that all vulcanizates degrade
in the same manner.   Tobolsky's conclusions are based on a similarity in re-
laxation rate of sulfur-based and sulfurless vulcanizates, on disparities in the
rate of stress relaxation when the polymers are different, and on the occurrence
of a maximum rate during the oxidation of a vulcanizate of an unspecified com-

position (but presumably containing sulfur). The supposed similarity in re-laxation of sulfur and sulfurless vulcanizates is not borne out by the present data and it does not necessarily follow that scission at crosslinks in, for example, butyl and natural rubber vulcanizates cured by the same system, should occur at similar rates. Even if scission involves crosslinks, aging might well occur as a co-oxidation reaction of chain elements and crosslinks with the scission of the latter being the predominant degradative reaction and also scission at crosslinks might involve scission of adjacent main chain elements rather than the crosslinks themselves. The stocks used by Tobolsky sometimes contained added antioxidant and were, in any case, unextracted so that they contained natural antioxidants or antioxidants added during the manufacture of synthetic polymers as well as products of vulcanization. It is, therefore, difficult to
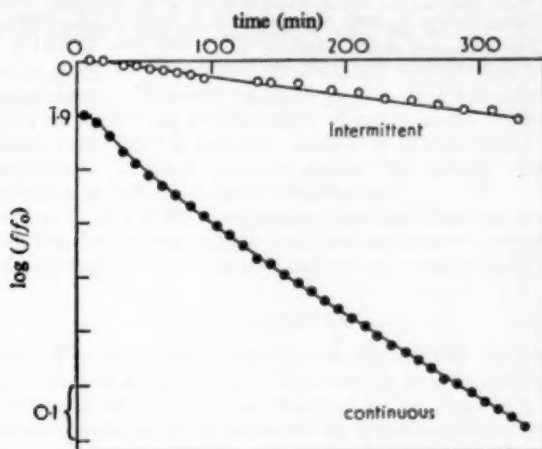
Fig. 8.—Intermittent and continuous stress relaxation of an extracted sulfenamide-accelerated vulcanizate of smoked sheet in air at 100° C.

interpret Tobolsky's data on fundamental lines or to compare them with the present results.

SYNOPSIS

The aging in the temperature range 80–100° C of natural rubber vulcanized by dicumyl peroxide, with a tetramethylthiuram disulfide recipe, a sulfenamide-sulfur recipe and by sulfur alone has been investigated by the method of stress relaxation.

The degradation of those vulcanizates prepared without elementary sulfur is autocatalytic and is retarded by small quantities of antioxidant. It is con-cluded that network breakdown in this case, as in the photochemical aging of peroxide vulcanizates previously investigated, is due to scission at random among the isoprene units of the polymer chains, occurring as part of an autox-idative reaction of the type which takes place in low-molecular-weight olefins.

The aging of the sulfenamide-sulfur and unaccelerated sulfur vulcanizates shows marked differences from that of the sulfurless systems. It does not show the characteristics of a chain reaction nor any other obvious similarity to olefin

autoxidation. No positive conclusions have been reached regarding the mechanism of aging of these vulcanizates.

ACKNOWLEDGMENT

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STRESS RELAXATION DURING THE PHOTOXIDATION
OF PEROXIDE CROSSLINKED RUBBER *

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The chemical reactions involved in the thermal and photochemical aging of natural rubber vulcanizates are largely unknown. Experimental difficulties have precluded direct chemical investigation owing to the insolubility of the crosslinked networks and the small extent of reaction required for a great deterioration in physical properties. Accordingly recourse has been made to physical measurement. Tobolsky et al. (e.g. Ref. (1)) have shown that the relaxation in stress on holding a rubber strip at constant extension during aging is a convenient experimental measure capable of interpretation in terms of network breakdown. In photochemical studies the opacity of conventional sulfur vulcanizates provides a further complication.

In the present work, the stress relaxation technique has been used in a study of the degradation by 365 mμ radiation of the comparatively transparent and chemically simple rubber networks obtained after crosslinking by organic peroxides[2].

EXPERIMENTAL

Apparatus.—The relaxometer used for measurement of the decay of stress was developed from that of Berry[3]. The tension in a rubber strip $3 \times 0.5 \times 0.02$ cm held at constant length as balanced by the force in a helical steel spring, whose extension could be measured by a vernier placed on the side of the instrument and viewed at right angles to the light beam. The clamps holding the rubber strip were on the face of the relaxometer away from the light source, light reaching the strip through the hollow framework of the instrument. This arrangement was necessary: for, unless the rubber in the regions of local strain around the clamps was shielded from the light, premature rupture occurred there.

A compact source lamp (250 W MBQ type of B.T.H. Ltd.) was used, the light being collimated by a quartz lens and passed through a quartz window into the thermostat. The jacket of the relaxometer was, however, of pyrex glass and resulted in a small reduction in light intensity. A Chance OV1 filter removed all but the 365 mμ line.

Preparation of peroxide vulcanizates.—Rubber containing the crosslinking agent, dicumyl peroxide, was cast as a film from benzene solution by the following technique. Deproteinized crepe[4] was extracted with hot acetone in a Soxhlet apparatus for 8 hr, dried under vacuum overnight and then dissolved to a 2% solution in benzene. 3% dicumyl peroxide on the weight of rubber was then added and the solution degassed. A film 0.2 mm thick was cast in a rectangular glass boat, floating on mercury and warmed by two infrared lamps, by drying three successive additions of the solution in a stream of nitrogen.

The boat with the dried film was sealed in a glass tube at 10^{-4} mm Hg pressure and heated at $140° \pm 0.5°$ C for 30 min.   The crosslinked film was acetone extracted, dried, cut into strips 0.5 cm wide and approximately 4 cm long, and stored in a vacuum desiccator.

Alternatively, the crosslinking agent, either 3% dicumyl peroxide or 2% di-t-butyl peroxide, was dissolved in the purified crepe in a small internal mixer[5], the limiting viscosity number of the rubber decreasing from 534 to 248 g^{-1} ml benzene.   The mixture was stored overnight under nitrogen and then introduced into a mold given a sheet $10 \times 10 \times 0.02$ cm.   Crosslinking was effected by heating at $140°$ C for 30 min under a pressure of 1 ton per sq in. The degradation during mixing was necessary for satisfactory flow in the mold. The sheets crosslinked by dicumyl peroxide were acetone extracted and dried. The sheets crosslinked by di-t-butyl peroxide were heated at $60°$ under 10^{-4} mm Hg pressure for 6 hr to remove unreacted peroxide and reaction products[2].

Incorporation of retarders and initiators.—These were introduced by swelling the rubber strips in ethyl acetate solutions overnight and subsequent drying. The concentrations recorded are based on the assumption that the amount of additive incorporated in the rubber corresponded to that originally contained in the solvent absorbed by the rubber.

RESULTS

Figure 1 shows two typical log stress against time curves for relaxation of

peroxide vulcanizates in oxygen at 760 mm Hg, (1a) having been obtained with a strip from a cast film vulcanized with dicumyl peroxide and (1b) with a strip from a molded sheet crosslinked by di-t-butyl peroxide.   The degradative reaction is strongly autocatalytic, the experimental points being fitted with good accuracy by the relation

$$f_0/f = (1 - a) + a \exp kt \qquad (1)$$

where f_0 and f are the tensions initially and at time t, and a, k are constants; the significance of this equation is discussed later.   Equation (1) may be rearranged to give a linear relation; for, selecting a convenient fixed time interval Δ and recording the tensions f_t at time t and $f_{t+\Delta}$ at time $t + \Delta$,

$$\ln f_0(f_{t+\Delta}^{-1} - f_t^{-1}) = kt + \ln \{a(\exp [k\Delta] - 1)\} \qquad (2)$$

Figure 1, accordingly, shows also the plots of $\log f_0(f_{t+\Delta}^{-1} - f_t^{-1})$ against t, from which values of a and k can be readily obtained.

No significant differences exist between the relaxation curves obtained with cast and molded strips or with strips crosslinked with the two different peroxides; neither did extraction of the di-t-butyl peroxide vulcanizates with acetone or ethyl acetate in addition to the normal removal of vulcanizing agent by pumping alter the rate of relaxation.

Light absorption.—Light absorption of unstretched strips was measured by a Hilger Uvispec spectrophotometer and allowance made by Fresnel's law for the reflection from the front surface and by Lambert's law for the change in thickness on stretching.   The absorption under experimental conditions of a typical cast dicumyl peroxide-vulcanized strip was initially 51% and changed by less than 2% after 50% degradation.   The absorption of molded films was some-
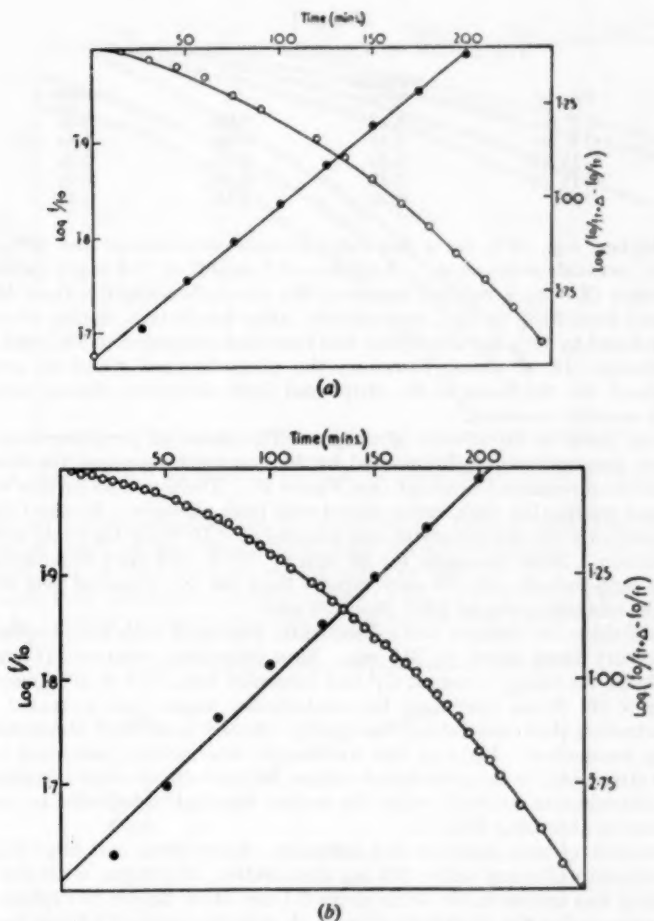
FIG. 1.—Photolytic stress relaxation of (a) a cast film crosslinked with dicumyl peroxide. O, log (f/f_0) against time; ●, log $\Delta(f_0/f)$ against time.   (b) a molded film crosslinked with di-t-butyl peroxide. O, log (f/f_0) against time; ●, log $\Delta(f_0/f_t)$ against time.
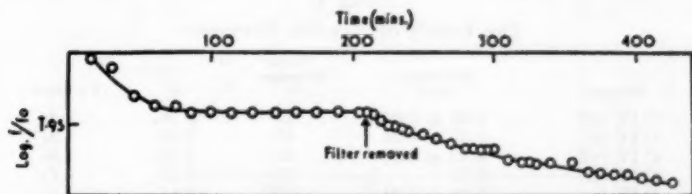
FIG. 2.—Photolytic stress relaxation in an atmosphere of nitrogen under 365 mμ and 313 mμ radiation.

TABLE I

THE EFFECT OF VARYING STRIP THICKNESS

Strip no.	Thickness (mm)	a	$k \times 10^4 \text{sec}^{-1}$
C V (i)	0.12	0.08$_1$	2.3$_9$
C V (v)	0.24	0.09$_7$	1.8$_5$
C IV (v)	0.30	0.14$_6$	1.6$_5$
C IV (i)	0.35	0.12$_4$	1.7$_7$
C III	0.50	0.14$_1$	1.5$_1$

what higher, e.g., 56% for a di-t-butyl peroxide vulcanizate and 67% for a dicumyl peroxide vulcanizate. Addition of 2-naphthol (7.0 mg/g rubber) or 1-naphthol (2.1 mg/g rubber) increased the absorption slightly, from 48% to 52% and from 51% to 55% respectively; after irradiation, during which the stress relaxed to 40% the absorption had increased somewhat to 62% and 64%, respectively. In all cases, therefore, the photochemical reactions occurred throughout the thickness of the strips and light absorption during aging remained sensibly constant.

Stress decay in the absence of oxygen.—The stress of a rubber strip in a nitrogen atmosphere and illuminated by 365 mμ light decreased for about 30 min and then remained constant (see Figure 2). There was no further relaxation upon refilling the relaxometer jacket with fresh nitrogen. Similar behavior was observed when the apparatus was pumped at $<10^{-4}$ mm Hg for $2\frac{1}{2}$ hr before illumination. After pre-aging for 40 min at 70° C and then illuminating *in vacuo* a strip initially relaxed more rapidly than one not pre-aged, but in both cases the relaxation ceased after about 30 min.

The strip under nitrogen was subsequently irradiated with wavelengths from the mercury lamp down to 313 mμ. Slow relaxation occurred (Figure 2). After 24 hr the elastic constant C_1^6 had increased from 0.75×10^5 dynes cm^{-2} to 1.18×10^5 dynes cm^{-2} and the unstretched length had increased 35%, demonstrating that crosslinking was readily effected in an inert atmosphere by 313 mμ irradiation. Light of this wavelength was strongly absorbed by the rubber strips, and, in the presence of oxygen, brought about a rapid degradation which ceased quite suddenly when the surface was highly degraded to produce a protective absorbing film.

Variation of strip thickness and extension.—Strips from cast films 0.35 mm thick relaxed uniformly under 365 mμ illumination, in oxygen, until the stress remaining was undetectable, while strips 0.1 mm thick tended to rupture at an early stage during the photolytic decay. A strip thickness of 0.2 mm has been employed in all experiments subsequently recorded. This ensured the absence of strip rupture during the first 60% of stress decay, yet there was illumination

TABLE II

THE EFFECT OF VARYING EXTENSION

Strip no.	Thickness (mm)	Initial extension %	a	$k \times 10^4 \text{sec}^{-1}$
C IV (iii)	0.35 ± 0.02	25	0.16$_4$	1.4$_9$
C IV (ii)	0.33 ± 0.02	50	0.12$_4$	1.9$_2$
C IV (viii)	0.40 ± 0.03	50	0.20$_4$	1.5$_7$
C IV (xi)	0.50	75	0.12$_4$	1.7$_4$
C IV (v)	0.30 ± 0.02	100	0.14$_5$	1.6$_5$
C IV (i)	0.35	100	0.11$_1$	1.7$_7$
C IV (iv)	0.32	150	0.14$_6$	2.0$_2$
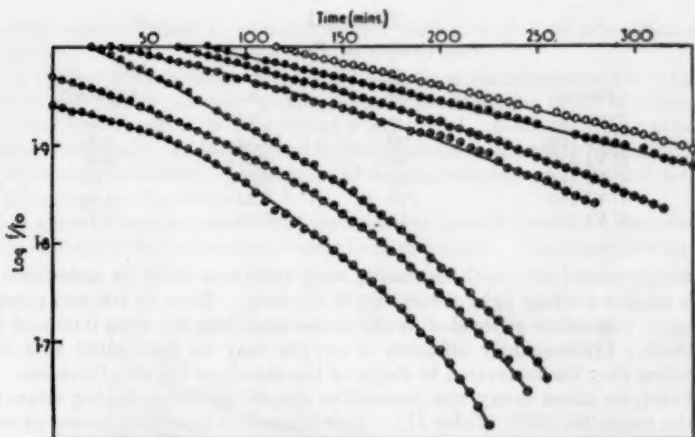
FIG. 3.—Effect of varying oxygen pressure upon stress relaxation under 365 mμ illumination.   ⊙, 29 mm O₂; ●, 47 mm O₂; ⊗, 71 mm O₂; ◑, 102 mm O₂; ◐, 204 mm O₂; ◓, 351 mm O₂; ◒, 760 mm O₂.

throughout the thickness of the extended strip.   Furthermore, the stress in such strips could be measured using springs of convenient dimensions, and the necessary rubber films could be readily cast and handled.

Variation of unstretched strip thickness in the range 0.1 to 0.5 mm brought about no marked change in the rate of relaxation (see Table I).   The trend
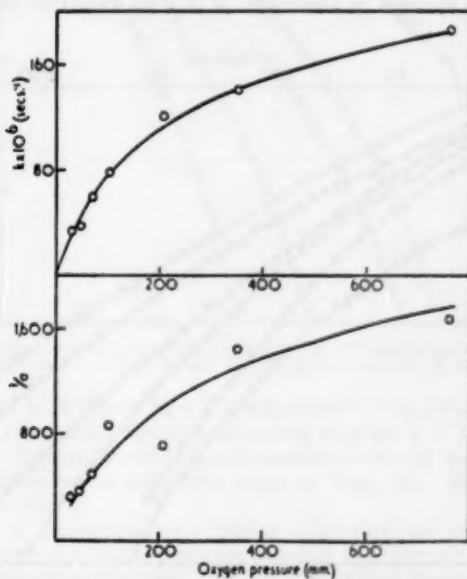
FIG. 4.—The variation of k and $1/s$ with oxygen pressure.

TABLE III

THE EFFECT OF PRE-AGING

Strip no.	Pre-aging (min)	a	$k \times 10^4 \sec^{-1}$
C VI (v)	0	0.15_1	1.2_8
C VI (vii)	60	0.15_1	1.3_1
C VI (vi)	90	0.21_7	0.9_8
C VI (viii)	135	0.30_2	1.0_7
C VI (ix)	195	0.21_7	1.5_6
C VI (x)	315	0.24_4	1.7_7

towards decreased rate with increasing strip thickness could be accounted for by the smaller average light absorption of the strip. Even at 100 mm pressure of oxygen, relaxation proceeded at about the same rate for films 0.09 and 0.27 mm thick. Consequently diffusion of oxygen may be discounted as a rate-controlling step for relaxation in strips of the standard 0.2 mm thickness.

Photolytic stress decay was insensitive also to extension during relaxation over the range 25–150% (Table II). Relaxation was somewhat slower at small extensions when the thickness of the extended strip was greater, presumably, because the average light absorption was again less in such cases. Subsequently all experiments were carried out at 100% extension.

Variation of rate with oxygen pressure.—A series of strips was irradiated at oxygen pressures varying from 30 to 760 mm (Figure 3). The values of k and $1/a$ both increased with oxygen pressure (Figure 4).

The effect of thermal pre-aging.—Unstretched rubber strips were heated at 70° C in air for varying times before being stretched and irradiated in oxygen. Such pretreatment had no marked effect upon the stress-time curves (Table III). The small changes in absorption of 365 mµ radiation occurring during
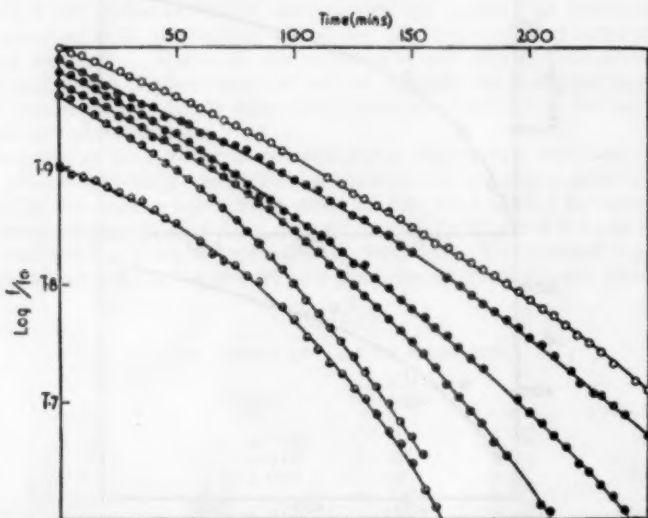
FIG. 5.—Photolytic stress relaxation in the presence of 2-naphthol. 2-Naphthol conc. (moles/base mole rubber) ×10⁴. ○, 23.6; ⊗, 12.7; ●, 8.2; ⊕, 2.5; ◐, 0.85; ◒, zero.

pre-aging were sufficient to account for the variation in k on relaxation after pre-aging.

The effect of phenolic antioxidants.—Photolytic stress relaxation was retarded by small amounts of phenolic antioxidants in the following order of efficiency: pyrogallol $\simeq$ 1-naphthol $\gg$ 2-naphthol $>$ resorcinol. *p*-Methoxyphenol has an unusual effect which can be ascribed to the production of a more potent retarder as illumination proceeds. The results of detailed studies using 2- and 1-naphthol are shown in Figures 5 and 6.

The effect of benzoin and benzoyl peroxide.—Figure 7 illustrates the effect of adding benzoin to the rubber strips prior to illumination. The relaxation param-
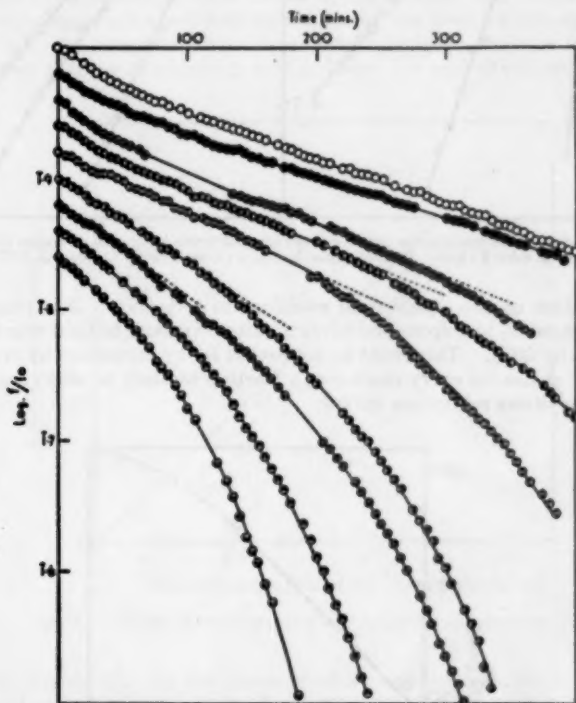
Fig. 6.—Photolytic stress relaxation in the presence of 2-naphthol. 1-Naphthol (moles/base mole rubber) $\times 10^4$. ⊙, 11.3; ●, 5.3; ⊗, 3.18; ◐, 2.35; ◔, 1.54; ◑, 1.21; ⊕, 0.54; ◓, 0.23; ◯, zero.

eters are $k = 370 \times 10^{-6}$ sec^{-1}, $a = 0.244$, in the presence of 0.536 mg/g rubber of the initiator, whereas for the untreated strip they are $k = 140 \times 10^{-6}$ sec^{-1} and $a = 0.471$. Benzoyl peroxide also increases the rate of decay, the form of the stress relaxation curves still being given by Eqn. (5). The effect was to increase k rather than a.

Development of permanent set.—During relaxation the strips developed permanent set, showing that the scission reaction is accompanied by a recombination or crosslinking reaction. The amount of this reaction can be estimated from the moduli of elasticity before and after relaxation measured by
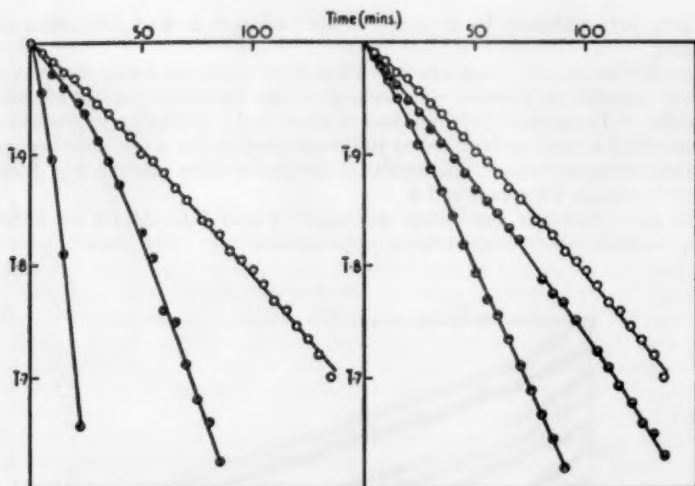
Fig. 7.—Photolytic stress relaxation in presence of benzoin and benzoyl peroxide. Benzoin (mg/g rubber), left: O, zero; ◑, 0.54; ●, 9.65. Benzoyl peroxide (mg/g rubber), right: O, zero; ◐, 0.57; ●, 4.93.

determinations of the equilibrium swellings in n-decane.[6] For example, the elastic constant C_1 had decreased by 40%, after exposure to light which reduced the tension by 50%. This could be accounted for by formation by crosslinking of 0.15 new chains for every chain cut, a fraction unlikely to affect seriously the shape of the stress relaxation curves.
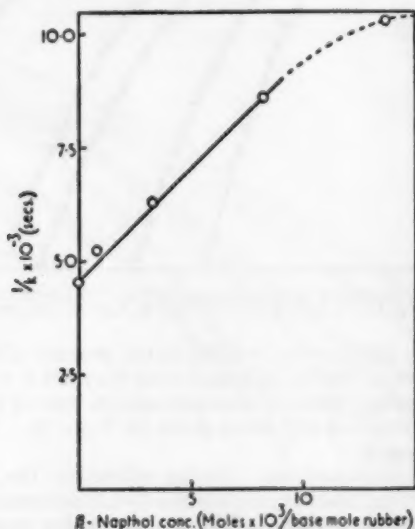
Fig. 8.—The variation of $1/k$ with 2-naphthol concentration.

DISCUSSION

That the degradation of the rubber networks under the influence of 365 mμ radiation is due to photo-initiated oxidation and not to direct photolytic scission is clear from the almost complete cessation of the reaction when oxygen is removed.   The degradation, in fact, shows the same qualitative features as those observed in the autoxidation of simple olefins[7].   First, both reactions are strongly autocatalytic.   Secondly, the photochemical degradation is also accelerated by the addition of the free radical producing initiators, benzoyl peroxide and benzoin, and is retarded in the same order of efficiency[8] by the addition of small amounts of phenols.

Addition of 2-naphthol to the rubber strips resulted in a reduction in the rate of photodegradation without alteration in the form of the stress-decay curves.   Over the range of concentrations for which the retarder was soluble in the rubber a linear relationship held between $1/k$ and the concentration of
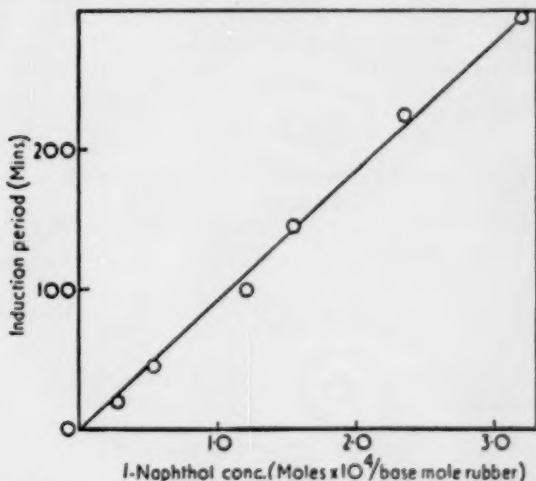
Fig. 9.—Variation of induction period with 1-naphthol concentration.

2-naphthol (Figure 8).   In the presence of 1-naphthol relaxation proceeded, after a short period of rapid decay, for some time at a low steady rate, which was almost independent of the 1-naphthol concentration, before the usual curved plot was obtained (Figure 6).   This induction period was proportional to the initial concentration of the 1-naphthol (Figure 9).

The experimental results provide little information on the primary photochemical reaction.   The absorption of 365 mμ radiation by the strips used in these experiments was much greater than by highly purified polyisoprene and was probably due to the remaining small quantity of nonrubber constituents. It may be that these absorbers are capable of acting as photosensitizers to the decomposition of hydroperoxides or, alternatively, that a small part of the light absorbed is actually absorbed by hydroperoxide directly and only this is effective in initiating the reaction.   Either of these alternatives could explain

the considerable increase in rate unaccompanied by any appreciable increase in absorption.

Similar suggestions to that made here of a scission reaction occurring as part of the autoxidative process have been made in the past to account for oxidative degradation of both vulcanized and unvulcanized polyisoprene. Farmer and Sundralingham[9] concluded that the degradation of unvulcanized rubber in ultraviolet light was due to a reaction of the hydroperoxide formed during the oxidation.

More recently, Morris[10] concluded from his rate data on the oxidation of gutta percha that scission occurred during the propagation steps of the oxidative chain reaction. Bevilacqua[11] has advanced a more detailed picture of decomposition of the diperoxide-hydroperoxy radical formed during the propagation steps. It is shown in the following paragraphs that decomposition either of hydroperoxide or of an intermediate radical can lead to a form of stress-time curve consistent with the experimental results.

It is assumed that the scission may occur at random at any point along the chains of isoprene units and that the crosslinks are also distributed at random along these chains. Then if $1/p$ is the average number of units liable to scission in a chain segment between two crosslinks, the number of chain segments containing x units is

$$N_x = N_0 p(1 - p)^{x-1} \tag{3}$$

where $N_0 = \sum_{x=1}^{x=\infty} N_x$ is the total number of chain segments.

After a fraction q of the links has been cut, the total number N of chain segments remaining uncut is

$$N = \sum_{x=1}^{x=\infty} N_0 p(1 - p)^{x-1}(1 - q)^x = \frac{N_0 p(1 - p)}{p + q - pq} \simeq \frac{N_0 p}{p + q}, \text{ since } p, q \ll 1 \tag{4}$$

The force f required to maintain a constant extension is proportional to N (cf. Ref. (1)) and thus

$$\frac{f_0}{f} = \frac{N_0}{N} = 1 + \frac{q}{p} \tag{5}$$

In thermal autoxidations of olefins the rate of formation of hydroperoxide obeys an autocatalytic relation

$$d[\text{ROOH}]/dt = k[\text{ROOH}], \tag{6}$$

where k is a pseudo constant dependent on the olefin concentration and the oxygen pressure. Photochemical autoxidations of highly purified olefins do not give such simple behavior because of a difference in order between the initiation and termination steps, the photo-initiation reaction being first order in hydroperoxide while the termination reaction is second order in radical species. Although the exact nature of the initiation reaction under the present conditions is unknown it is likely to be likewise first order in hydroperoxide. Moreover, the introduction of the retarder 2-naphthol resulted in no change in form of the stress-time curves, and since the additional termination reaction resulting is

almost certainly first order in radical species, it is concluded that in its absence the termination reaction is also predominantly first order, being due to adventitious retarder already present in the rubber strips.   If this is the case, Eqn. (6) will still be correct.

Assuming that scission occurs as an alternative to a propagation step, the number of cuts will be proportional to the amount of oxygen taken up, i.e.,

$$q = \epsilon([ROOH] - [ROOH]_0) \tag{7}$$

and thus

$$dq/dt = \epsilon k[ROOH]_0 + kq \tag{8}$$

Integration then gives Eqn. (1) with

$$a = \epsilon[ROOH]_0/p \tag{9}$$

If on the other hand it is assumed that scission is due to a first order breakdown reaction of hydroperoxide.

$$dq/dt = k_2[ROOH] \tag{10}$$

but the form of (6) will be unchanged.   Then from (6) and (10)

$$d^2q/dt^2 = kdq/dt \tag{11}$$

or

$$dq/dt = k_2[ROOH]_0 + kq \tag{12}$$

which differs from (8) only in the constant term and gives the same integrated form (1) with, however,

$$a = k_2[ROOH]_0/kp \tag{13}$$

which now involves k as a divisor; this is of course due to the fact that in this case the initial rate of degradation, $dq/dt = akp$, must be independent of the rate of oxidation.

The present results do not unequivocally favor either of the alternative mechanisms.   Increase in initial rate of relaxation by benzoin or benzoyl peroxide (Figure 7) is to be expected if degradation occurs during the propagation cycle.   However, the approximately constant initial rate of degradation at different oxygen pressures (Figure 3) and retarder concentrations (Figure 5) can be accounted for by hydroperoxide decomposition.   It is possible that both mechanisms are operative, giving the observed predictions of both under the appropriate experimental conditions.

SYNOPSIS

Stress relaxation under the influence of 365 mμ radiation at 25° C of natural rubber crosslinked with organic peroxides shows the degradative process to be autocatalytic, the presence of oxygen being essential.   The stress against time data and the effects of phenolic retarders and catalysts can be represented by a relationship derived on the assumption that the degradation is a reaction in an autoxidation mechanism similar to that observed for simple olefins.

ACKNOWLEDGMENT

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CIS–TRANS ISOMERIZATION IN NATURAL POLYISOPRENES *

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The *cis* and *trans* isomers of many simple olefins and conjugated polyolefins can be interconverted by the action of heat, light, and various catalysts, and in many such systems the changes in geometric configuration can be readily followed and the isomers separated and identified.

Previous attempts[1, 2] to isomerize natural rubber and gutta-percha by treatment with ultraviolet light and various chemicals gave no detectable *cis-trans* isomerization, and in general configurational changes in unconjugated polyolefins have been unknown until recently when Golub[3] converted the *cis*-1,4 units in polybutadiene into the corresponding *trans* units. This isomerization was achieved by irradiation of the *cis*-polymer with ultraviolet light in the presence of various organic bromides and sulfur compounds, but apparently this method did not isomerize natural rubber.

In attempts to retard the rate of crystallization of natural rubber at moderately low temperatures—i.e., $-10°$ to $-40°$ C—by the attachment of side groups which would interfere with the molecular packing, it was observed that very small amounts of thiol acids were remarkably effective[4]. This suggested that structural changes other than simply the attachment of side groups were occurring in the polyisoprene molecule. Recently it was found that thiol acids could interconvert the *cis* and *trans* forms of a simple trialkyl ethylene—e.g., 3-methylpent-2-ene—and subsequently, the isomerization of natural rubber and gutta-percha by these reagents was also observed[5]. Following this, natural rubber, gutta-percha, squalene and *cis* and *trans* forms of 3-methylpent-2-ene have also been isomerized by treatment with sulfur dioxide and allied compounds[5]; this work, including an investigation of the physical properties of the vulcanizates obtained from some of the isomerized polyisoprenes, is described in the present paper.

ISOMERIZATION OF *CIS*- AND *TRANS*-3-METHYLPENT-2-ENE

A mixture of the geometric isomers of 3-methylpent-2-ene was prepared as previously described[6]. Fractional distillation gave the pure *cis* and *trans* isomers[7], b.p. 67.5° C at 758 mm, n^{20}D 1.4021, and b.p. 70.0° C at 758 mm, n^{20}D 1.4050, respectively, which had infrared spectra identical with the API[8] spectra, provided that the API assignments of configuration are reversed as previously suggested[7]. Synthetic mixtures of the two isomers in carbon disulfide solution were analyzed spectroscopically in the infrared using a band at 750 cm^{-1}, present only in the spectrum of the *trans* isomer, to give results within $\pm 2\%$ of the known composition; this calibration was applied to the isomerized samples. The spectra of these samples were consistent with the presence of the two

methylpentene isomers only, difference spectra confirming that the alternative
isomer is the only product of the reactions.

Isomerization was carried out by heating 1 ml samples of the *cis* and *trans*
olefins with 3% by weight of thiolbenzoic acid, dibenzoyl disulfide and buta-
diene sulfone. (Butadiene sulfone was frequently used instead of sulfur di-
oxide, since it quantitatively liberates the latter reagent at temperatures above
130° C). The isomerized olefin was freed from isomerizing reagent by dis-
tillation and the *cis* and *trans* contents determined by spectroscopic analysis.
The results are as shown in Figure 1. With the sulfone at 140° C, an equilib-
rium of 57% *trans* isomer was reached in about 20 hours. With thiolbenzoic
acid and dibenzoyl disulfide at 140° C, equilibrium was not reached, but the
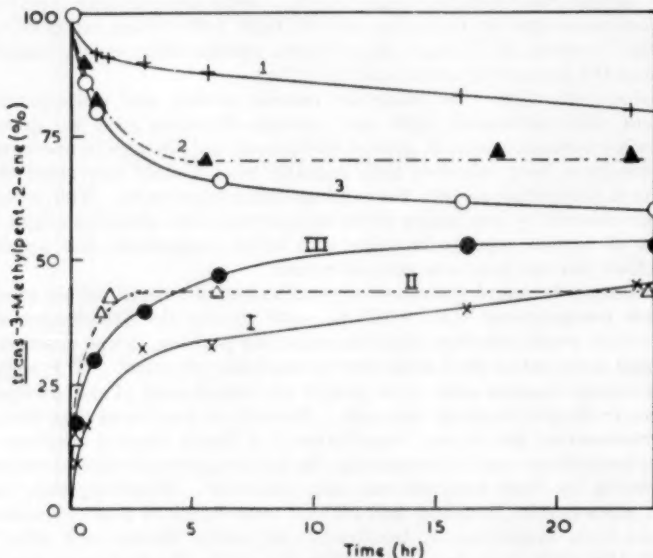
Fig. 1.—Isomerization of *cis*- and *trans*-3-methylpent-2-ene at 140° C by thiolbenzoic acid, dibenzoyl
disulfide, and butadiene sulfone. 1, I, dibenzoyl disulfide; 2, II, thiolbenzoic acid; 3, III, butadiene sulfone.

mean values across the gaps indicated the same equilibrium as obtained with
the sulfone.

ISOMERIZATION OF SQUALENE

This hexa-isoprene was obtained from shark liver oil[9]; on treatment with
thiourea it gave the crystalline clathrate compound from which all-*trans*
squalene was regenerated[10] in 85% yield. Its spectrum was identical with those
previously published[10, 11]. Treatment of the all-*trans* squalene with sulfur
dioxide or butadiene sulfone (3%) for 24 hours at 140° C gave a product which
was identical in molecular weight and elementary analysis with the starting
material but which otherwise differed as follows:

(i) It did not crystallize on cooling to −78° C; (ii) it gave no precipitate
with thiourea at room temperature (all-*trans* squalene gives an immediate
precipitate of the clathrate compound); (iii) with thiourea at 2° C it gave a

yield of clathrate compound which corresponded to 11% of all-*trans* squalene; (iv) its infrared spectrum differed from that of all-*trans* squalene and was consistent with the presence of *cis* double bonds, no estimate of the latter being possible, however, since no standard is available for all-*cis* squalene; and (v) a
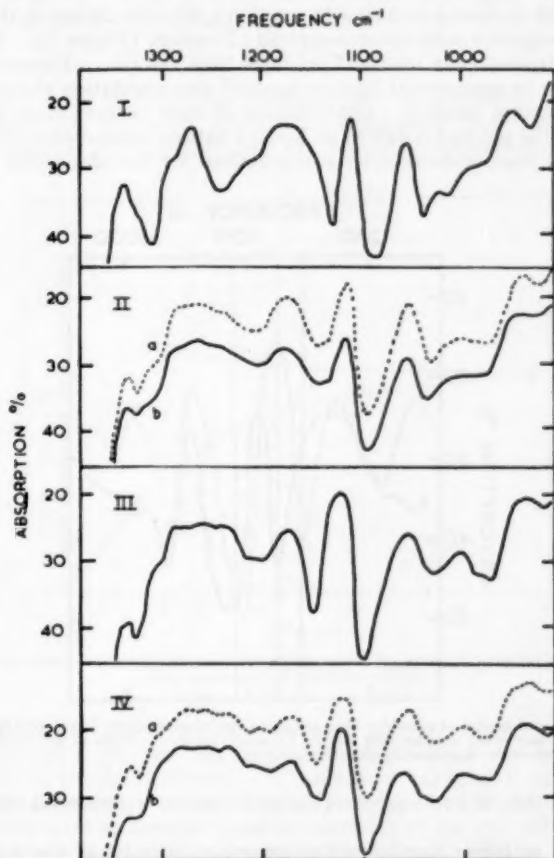
Fig. 2.—Infrared spectra of natural rubber and gutta-percha before and after isomerization. (Cell lengths 1.0 mm.). I, natural rubber (in carbon disulfide 2% w/v); II, a, Gutta-percha treated for 24 hours at 140° C with sulfur dioxide (in carbon disulfide 2% w/v); II, b, Natural rubber treated for 24 hours at 140° C with sulfur dioxide (in carbon disulfide 2% w/v); III, Gutta-percha (in carbon disulfide 2% w/v); IV, a, Gutta-percha (in carbon disulfide 1% w/v); IV, b, Difference spectrum of natural rubber treated for 10 hours at 140° C with sulfur dioxide (in carbon disulfide 2% w/v) against natural rubber (in carbon disulfide 1% w/v); II, b, and IV, b, are displaced by 5% (absorption) for clarity.

difference spectrum against all *trans* squalene resembled that of natural rubber, whereas that of all *trans* squalene is very similar to that of gutta-percha. These facts clearly suggest that isomerization of the squalene has occurred and, assuming equilibrium at each double bond as 60% *trans*, then the expected yield of all *trans* isomer is $0.6^4 \times 0.85 \times 100 = 11\%$—i.e., as found in (iii).

ISOMERIZATION OF NATURAL RUBBER AND GUTTA-PERCHA

When natural rubber and gutta-percha are in the amorphous state their infrared spectra are very similar but not identical (Figure 2). Treatment of thin sheets (0.5 to 2 mm thick) of the unvulcanized polymers with sulfur dioxide at 140° C gave products whose infrared spectra revealed structural changes which increased with time of reaction until, after 24 hours, the products from both polymers were spectroscopically identical (Figure 2). The formation of spectroscopically identical products from the two polyisoprenes which are known to be geometrical isomers implies[12] stereomutation of each polymer to an equilibrium mixture. Confirmation of such isomerization is that the spectrum of the product obtained on heating natural rubber with sulfur dioxide for 10 hours was identical, after compensation for the absorption of natural
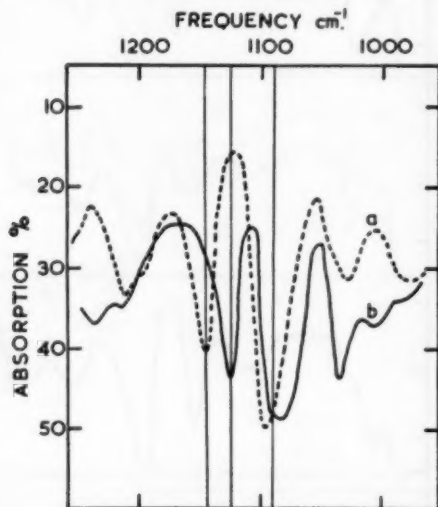
FIG. 3.—Infrared spectra of natural rubber and gutta-percha showing the bands used for the analysis of mixtures and isomerized samples (cell lengths 1.0 mm): (a) gutta-percha in carbon disulfide, 2.5% (w/v); (b) natural rubber in carbon disulfide, 2.5% (w/v).

rubber, with that of gutta-percha (Figure 2), no other structural change being detectable.

In order to follow this isomerization quantitatively, it was necessary to establish a method[5] which was more sensitive than those already existing for the determination of the microstructure of polyisoprenes[12-15] and which would allow the analysis of less than 5% isomerization. Examination of the spectra of carbon disulfide solutions of highly purified natural rubber and gutta-percha indicated that they possessed characteristic bands at 1125 and 1145 cm^{-1}, respectively[12], and that at 1090 cm^{-1} the absorption of both polymers is identical (Figure 3). Application of the Beer-Lambert law to the absorption of mixtures of natural rubber and guta-percha at these frequencies leads to the expression

$$f_g = \frac{K - R}{K_1 R + K_2}$$

where f_g is the weight fraction of gutta-percha in the mixture, and:

$$R = (\log T^{M}_{1150} - \log T^{M}_{1280})/(\log T^{M}_{1170} - \log T^{M}_{1280})$$

$$K = (\epsilon^{N}_{1280} - \epsilon^{N}_{1145})/(\epsilon^{N}_{1280} - \epsilon^{N}_{1135})$$

$$K_1 = (\epsilon^{N}_{1155} - \epsilon^{G}_{1155})/(\epsilon^{N}_{1280} - \epsilon^{N}_{1155})$$

$$K_2 = (\epsilon^{N}_{1145} - \epsilon^{G}_{1145})/(\epsilon^{N}_{1280} - \epsilon^{N}_{1155})$$

Here, ϵ and T refer to extinction coefficient and transmittance, respectively, and the super- and subscripts indicate the component (N = natural rubber, G = gutta-percha, M = mixture) and the frequency, respectively.
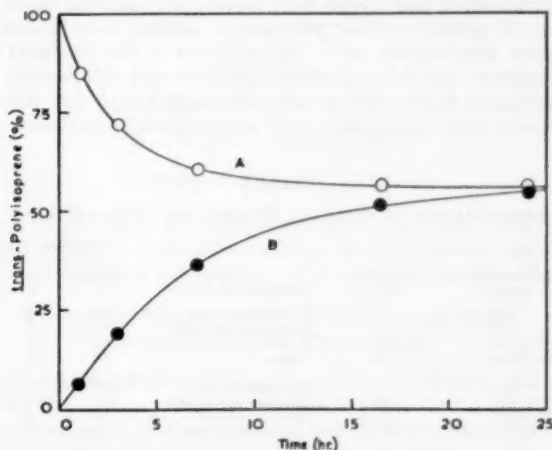
FIG. 4.—Isomerization of natural rubber and gutta-percha at 140° C by sulfur dioxide. A. Gutta-percha, B. Natural rubber.

This expression is independent of the total polymer concentration and cell length, which are important considerations in the handling of viscous solutions of polymers in a volatile solvent. A calibration curve of R against f_g was constructed, after separate determination of K, K_1, and K_2 had been made; the curve was used to analyze synthetic mixtures of the two polymers. The validity of this expression is confirmed by the following results:

f_g (prepared)	0.23	0.41	0.49	0.60
f_g (found)	0.22	0.40	0.49	0.60
	0.24	0.41	0.50	0.60

In order to obtain results of this accuracy, it is essential to determine the transmittances at the frequencies chosen and not at the observed maxima which shift by several wave numbers, due to band overlapping. Chloroform (<0.1% w/v) was added to give a medium intensity band at 1210 cm^{-1} to ensure that the results would be unaffected by slight changes in instrument calibration. Absorbances were then determined at frequencies relative to this band and not to the instrument fiducial marks.

Although results obtained for solutions with values of f_g outside the range shown above indicated an accuracy within ± 0.05, analyses were performed only on solutions with values of f_g between 0.2 and 0.6. This was achieved (in the case of slightly isomerized samples) by the addition of the appropriate pure polyisoprene, the difference in the calculated and observed values of f_g giving the isomeric constitution of the sample. The detailed stereochemical results are as shown in Figure 4. It can be seen that after 24 hours' treatment with sulfur dioxide at 140° C both polymers are converted into products which contain 57% of *trans* double bonds and 43% of *cis* double bonds, a *cis/trans* ratio which corresponds to the equilibrium composition for the *cis* and *trans* isomers of 3-methylpent-2-ene at the same temperature.

Isomerization of the two polyisoprenes was also achieved in the following ways: (i) unvulcanized thin sheets were heated in evacuated tubes with butadiene sulfone; (ii) solutions of the polymers in benzene were heated with butadiene sulfone or thiolbenzoic acid; (iii) solutions of the polymers in benzene containing diphenyl disulfide, dibenzoyl disulfide and thiolbenzoic acid, were irradiated in quartz flasks with a mercury vapor lamp; (iv) natural rubber latex was treated with thiolbenzoic acid as previously described[4]; and (v) by

TABLE I
ISOMERIZATION OF NATURAL RUBBER AND GUTTA–PERCHA

Polymer	Isomerization reagent	Amount, wt, %	Reaction conditions	Reaction Temp, ° C	Time, hr	Constitution of product, % *trans* form
Natural rubber	BS[a]	3	Benzene solution	140	24	12
	BS[a]	3	Unvulcanized sheet	140	7	43[b]
	PhCOSH	0.16	Latex	60	5	6
	PhCOSH	1.28	Latex	60	5	22
Gutta-percha	BS[a]	3	Benzene solution	140	24	81
	BS[a]	3	Unvulcanized sheet	140	24	60
	PhCOSH	5	Benzene solution	25	2	82
	PhCOSSCOPh	25	ultraviolet light	25	2	81

[a] BS = butadiene sulfone.
[b] Product soluble after grinding on a mixing mill.

treatment of thin sheets of the vulcanized polymers with sulfur dioxide. The results obtained with the soluble products are given in Table I; insoluble products were obtained from natural rubber by method (iii) and consequently they could not be spectroscopically analyzed, but their slower rate of crystallization at $-26°$ C (for significance of this see later) indicated that isomerization had also occurred in these materials.

MECHANISM OF ISOMERIZATION OF POLYISOPRENES BY THIOL ACIDS AND SULFUR DIOXIDE

The isomerization of the polyisoprenes and the simple olefins by thiol acids probably occurs via a reversible step in the addition reaction[16, 17] as indicated below. The addition takes place via a free radical process; in step 2 the thioacyl radical adds to the double bond giving a composite radical which may either react with more thiol acid giving the adduct as in (3), or it may regenerate either a *cis* or *trans* double bond depending upon its configuration at the time of thioacyl radical loss. If step 2 occurs much more rapidly than step 3, then many double bonds will be isomerized for each molecule of thiol acid added.

$$RCOSH \xrightarrow{-H} RCOS\cdot \tag{1}$$

$$\begin{array}{c} CH_3 \quad H \\ C==C + RCOS\cdot \rightleftharpoons \cdot C\text{---}C\text{---}SCOR \rightleftharpoons \\ \text{---}CH_2 \quad CH_2\text{---} \end{array}$$

cis   composite radical

$$\begin{array}{c} CH_3 \quad CH_2\text{---} \\ C==C + RCOS\cdot \\ \text{---}CH_2 \quad H \end{array} \tag{2}$$

trans

+

RCOSH

$$\begin{array}{c} CH_3 \quad H \\ H\text{---}C\text{---}C\text{---}SCOR + RCOS\cdot \\ \text{---}CH_2 \quad CH_2\text{---} \end{array} \tag{3}$$
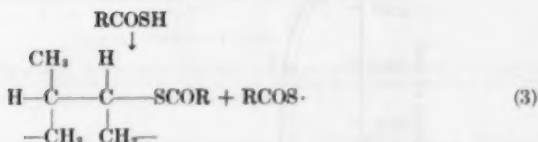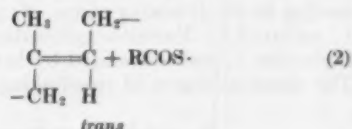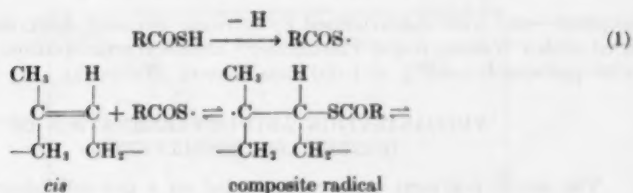
Isomerization by sulfur dioxide presumably occurs via a similar "on-off" reaction at the double bond, but free radicals are not involved since the rate of isomerization appears to be insensitive to free radical catalysts and inhibitors[18].

PROPERTIES OF GUM VULCANIZATES FROM
ISOMERIZED POLYISOPRENES

Gutta-percha and milled natural rubber (Highly Purified Rubber, United States Rubber Co.) were extracted with hot acetone for 24 hours, dried, and isomerized by heating in an atmosphere of sulfur dioxide at 140° C. Thirteen polyisoprenes including two controls of untreated natural rubber and gutta-percha were made—i.e., covering the range from 100% *cis* to 100% *trans* poly-

TABLE II

PHYSICAL PROPERTIES OF ISOMERIZED POLYISOPRENES AND CONTROLS

Reaction time, hr with SO₂ at 140° C		[η]ᵃ	Gelᵇ content, %	Bulk viscosity	Unsaturation, %	*trans* Content, %
From natural rubber	0	3.64	0	44	95	0
	0.5	3.60	0	46	97	5
	1.5	3.50	0	43	97	9
	3	3.31	0	46	98	21
	5	3.54	0	47	97	28
	8	4.24	6.0	68	97	39
	24	4.54	8.8	80	98	56
From gutta-percha	0	1.98	0	23	100	100
	0.5	2.26	0	22	97	95
	1.5	2.14	0	26	99	86
	3	1.67	0	32	104	74
	6	2.19	0	38	101	63
	24	1.65	4.0	40	—	58

ᵃ [η] is intrinsic viscosity expressed in grams per 100 ml.
ᵇ Wt. % of polymer insoluble in n-decane after 48 hr swelling at 25.0° C.

isoprene—and were characterized by intrinsic viscosity, bulk viscosity [measured with a Wallace Rapid Plastimeter[19], chemical unsaturation [by treatment with perbenzoic acid[20]], and *cis/trans* content (Table II).

VULCANIZATION AND DETERMINATION OF
DEGREE OF CROSSLINKING

The above polymers were compounded on a two-roll laboratory mill according to the following recipe, A: polyisoprene 100; zinc oxide 5; stearic acid 1; sulfur 2.5; N-cyclohexylbenzthiazolyl-2-sulfenamide 0.7; phenyl-2-naphthylamine 1; and vulcanized by heating in a press at 140° C for 30 minutes. The chemical degree of crosslinking in these vulcanizates was calculated from

FIG. 5.—Tensile and modulus properties of gum vulcanizates from isomerized natural rubber and gutta-percha. 1, vulcanizates from natural rubber ($10^4/2M_c = 0.35 \pm 0.04$); 2, vulcanizates from natural rubber ($10^4/2M_c = 0.73 \pm 0.21$); 3, vulcanizates from gutta-percha ($10^4/2M_c = 0.75 \pm 0.12$); 4, 100% modulus for vulcanizates of 1 and 3.

their equilibrium volume swelling values (V_r), which were determined in n-decane at 25° C[21, 22]. (This calculation assumes that the relationship between volume swelling and degree of crosslinking is the same as for natural rubber accelerated vulcanizates, and that the intrinsic viscosity-molecular weight relationship is the same as for natural rubber.) The values found showed that the degree of crosslinking had a tendency to increase with increasing *trans* content, and that the degree of crosslinking was less variable in the vulcanizates obtained from isomerized gutta-percha ($10^4/2M_c = 0.75 \pm 0.12$) than in those obtained from isomerized natural rubber ($10^4/2M_c = 0.73 \pm 0.21$). A series of vulcanizates with less variable degrees of crosslinking ($10^4/2M_c = 0.35 \pm 0.04$) was obtained from the isomerized natural rubbers by varying the amount of sulfur and accelerator used for their vulcanization.
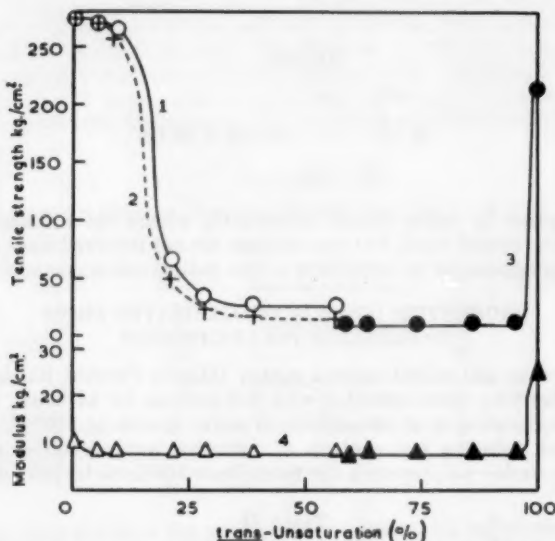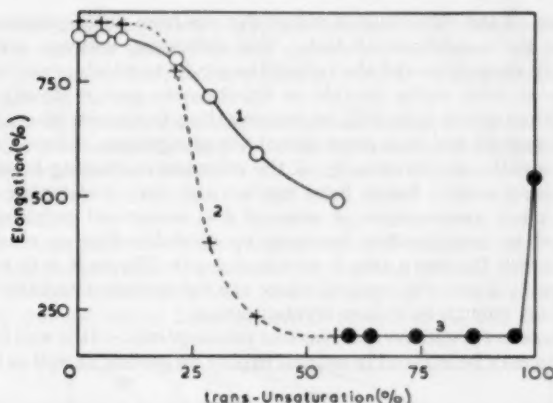
Fig. 6.—Elongation at break of gum vulcanizates from isomerised natural rubber and gutta-percha. 1, vulcanizates from natural rubber ($10^5/2M_c = 0.35 \pm 0.04$); 2, vulcanizates from natural rubber ($10^5/2M_c = 0.73 \pm 0.21$); 3, vulcanizates from gutta-percha ($10^5/2M_c = 0.75 \pm 0.12$).

Physical testing.—Bulk viscosities were measured at 100° C on a Wallace Rapid Plastimeter[19]. The tensile strengths and stress-strain properties recorded in Figures 5 and 6 and in Table III were measured on a Goodbrand testing machine by extending Type C British Standard 903 dumb-bells at 600% per minute. Rate of crystallization was measured by means of the relaxation of stress in a vulcanized test piece extended 150% and maintained at −26° C (at which temperature the rate is maximal). The time for reduction of stress by a factor of 2 has been shown[22] to be an accurate measure of the time for half the primary crystallization to be achieved; stress half life is thus an inverse measure of rate of crystallization.

Tensile and stress-strain properties of gum vulcanizates.—Figures 5 and 6 show that disruption of the regularity of structure in natural rubber and gutta-percha by isomerization markedly affects the physical properties of their vulcanizates, and in a similar manner to that found by Kraus[24] for a series of *cis* and *trans* isomers of polybutadiene. Modulus at 100% elongation (Figure 5) is constant for all the vulcanizates except vulcanized gutta-percha—this is as

TABLE III

PHYSICAL PROPERTIES OF ISOMERIZED NATURAL RUBBER
COMPARED WITH SMOKED SHEET

| | Isomerized natural rubber[a] | | | | | |
| Type of rubber | From latex and thiol benzoic acid | | From dry rubber and sulfur dioxide | | Smoked sheet | |
Vulcanization system	Recipe A	Recipe B[b]	Recipe A	Recipe B	Recipe A	Recipe B
Tensile strength, kg/cm²	254	223	262	243	275	242
Elongation at break, %	790	500	700	480	700	390
Modulus at 300%, elongation, kg/cm²	15	120	23	138	22	169
Modulus at 100%, elongation, kg/cm²	8	16	8	38	10	31
Shore hardness	43	67	44	71	45	70
Mooney scorch time[c] at 120° C, min	22	12	30	16	32	16

[a] Contained ~6% *trans* double bonds and crystallized > 500 times slower at −26° C than normal natural rubber.
[b] As for Recipe A with the addition of 45 parts of Philblack O.
[c] Time required to reach a five-point rise above the minimum on a Mooney viscometer.

expected since all the vulcanizates except the one from gutta-percha are amorphous under the conditions of test. The difference between gutta-percha which is partly crystalline and the rubberlike products which are obtained from it by treatment with sulfur dioxide or thiolbenzoic acid is clearly shown in Figure 7. When about 5 to 10% of isomerization has taken place, the tensile strengths (Figure 5) and to a lesser extent the elongations at break (Figure 6) begin to fall rapidly, and eventually all the polymers containing between about 25 to 95% *trans* double bonds have similar and very low tensile strengths. Preliminary x-ray examination of some of the isomerized polyisoprenes has indicated that as isomerization increases so crystallization on stretching decreases; and hence the sharp drop in tensile strength (Figure 5) is to be expected since presumably a point is reached where the vulcanizate breaks before it can be stretched far enough to induce crystallization.

Low temperature properties of isomerized polyisoprenes.—It is well known that crystallization may be induced in natural rubber by cooling as well as by stretch-
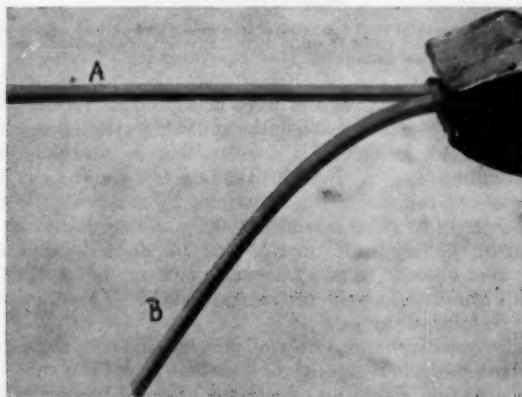
Fig. 7.—Rubber like properties of isomerized gutta-percha. A. vulcanized normal gutta-percha; B, vulcanized gutta-percha after treatment with sulfur dioxide for 30 minutes at 140° C.

ing and that the former property is disadvantageous since the material gradually becomes inelastic. In fact natural rubber vulcanizates under strain at temperatures from −10° to −40° C crystallize rapidly, becoming harder and losing their flexibility in a matter of a few hours or days depending on the service conditions and the type of vulcanization system employed. In this connection an investigation of the crystallization properties at low temperatures of the isomerized polyisoprenes has given some interesting results. For example, measurement of the rate of crystallization at −26° C of the products obtained by treatment of natural rubber with sulfur dioxide at 140° C for short periods —i.e., ∼ 1 hour—or by treatment of natural rubber latex with 0.16% thiolbenzoic acid[4] revealed that they crystallized several hundred times slower than normal rubber (Figure 8). Moreover, the tensile and stress-strain properties recorded in Figures 5 and 6 indicated that the products at this level of isomerization—i.e., containing ∼ 6% *trans* double bonds—were very similar in strength properties to ordinary natural rubber, and a more detailed investigation of their physical properties (Table III) has confirmed this. Therefore, for

uses at low temperatures these slightly isomerized rubbers possess a distinct advantage over normal natural rubber, since when vulcanized by recipe A, the latter would lose its elasticity in a few days at $-26°$ C whereas the former would retain its elasticity for many years.

Preparation of crystallization inhibited natural rubber.—The isomerization of natural rubber can be readily carried out in the laboratory either by treatment of dry rubber with sulfur dioxide or by reaction of thiol acids with latex, but for commercial scale preparations it has been found more convenient to use butadiene sulfone. In this way a process has been developed whereby the slightly isomerized rubber which crystallises several hundred times slower than normal natural rubber can be produced by heating natural rubber for a few minutes at 160° C with ∼ 2% of butadiene sulfone[25]. This reaction can be conveniently carried out in internal mixers or extruders, and the product so
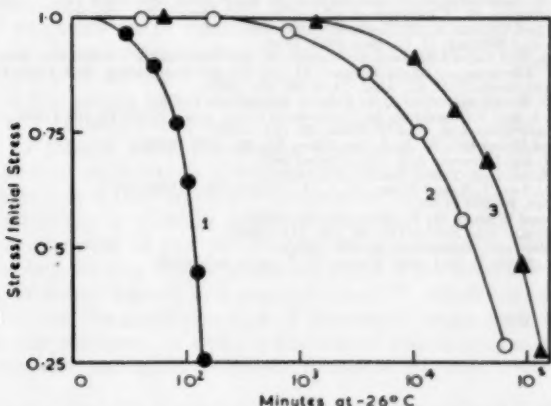
Fig. 8.—Decay in tension of vulcanized rubbers stretched 150% at −26° C and compounded and vulcanized as follows: polyisoprene 100; zinc oxide 5; stearic acid 2; tetramethylthiuram disulfide 4; phenyl-2-naphthylamine 1, heated for 40 minutes at 140° C; 1, normal natural rubber; 2, natural rubber treated with sulfur dioxide for 45 minutes at 140° C; 3, natural rubber from latex treated with 0.16% thiolbenzoic acid.

obtained has properties virtually identical with those given for the sulfur dioxide-treated rubber in Table III.

SYNOPSIS

Natural rubber, gutta-percha, squalene, and *cis* and *trans* 3-methylpent-2-ene undergo double bond isomerizations on treatment with thiol acids, sulfur dioxide, and allied reagents. Natural rubber and gutta-percha, and the two pentenes have been converted into equilibrium mixtures of similar isomeric composition (57% *trans* at 140° C). Isomerization was detected and quantitatively estimated by infrared spectroscopy.

Examination of a series of isomerized polyisoprenes covering the range from 100% *cis* to 100% *trans* has shown that configurational changes in the double bonds of natural rubber and gutta-percha cause marked changes in the physical properties of their vulcanizates. The product obtained from natural rubber containing about 6% *trans* double bonds is particularly interesting; although its tensile and stress-strain properties are very similar to those of

normal natural rubber, its rate of crystallization at low temperatures is several
hundred times slower.

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THE MUTUAL SOLUBILITY OF POLYMERS.
V. MECHANOCHEMICAL BLENDING *

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It is well known that mixtures of polymers may be produced by various methods. Nevertheless all this multiplicity of mixtures may be conveniently divided into two large groups. In the first we may put mixtures of any origin, if only no chemical alteration in the molecules takes place on mixing. Such mixtures of polymers are in essence either true solutions of a polymer in a polymer or else microheterogeneous systems; they have been considered in detail by one group of workers[1-5] and also by a second group[6-10]. (It may be noted that in the papers by Alekseenko and coworkers there is an erroneous proposition of a decisive part played by the polarity of polymers in their compatibility. As follows from the theory developed by one of the present authors[1-5], mutual solubility is determined by the thermal effect of mixing, which depends only partly upon the polarity of the polymers being mixed). In the second group of polymer mixtures there fall mixtures produced with simultaneous alteration of the structure of their molecules. With intensive mechanical action the long chains of the molecules of the polymers being mixed are split up, as is well known, in macromolecules[11-15], which combine one with another or initiate the polymerization of monomeric compounds, if these are contained in the polymer. A striking example of this type of mixture is that of block polymers and graft polymers produced by means of mechanical action[16-20].

The recently discovered phenomenon of chemical flow[21-23] is directly connected with the possibility of producing a mixture of the second type even from spatially crosslinked initial polymers.

Thus a mixture of two polymers may be produced in at least three different forms: a true solution of polymer in polymer, a microheterogeneous mixture of various sorts of chain molecules (compatibility without mutual solubility) and a mechanochemically modified mixture of chain molecules (block copolymers). The dependence of the properties of the two first forms of mixture upon the composition and structure of the mixed polymers has been the subject of investigation, while the dependence of the properties of mixtures produced by mechanochemical methods upon the composition of the initial polymers and the processing routine has as yet been little investigated and had hardly been compared with the properties of mixtures of the same composition but produced by mixing of the molecules without chemical change. The purpose of the present investigation is to establish the basic data in this field.

OBJECTS AND METHOD OF INVESTIGATION

For experiment we selected mixtures of butadiene rubber (SKB) with butadiene-styrene rubber (SKS-30A), since it has already been shown[1-4] that

systems of this kind possess a number of anomalies, while vulcanizates based on a combination of these rubbers are microheterogeneous. Since we have previously studied SKS-30 rubber, we repeated analogous investigations for mixtures of SKB, not containing antioxidants, with SKS-30A.
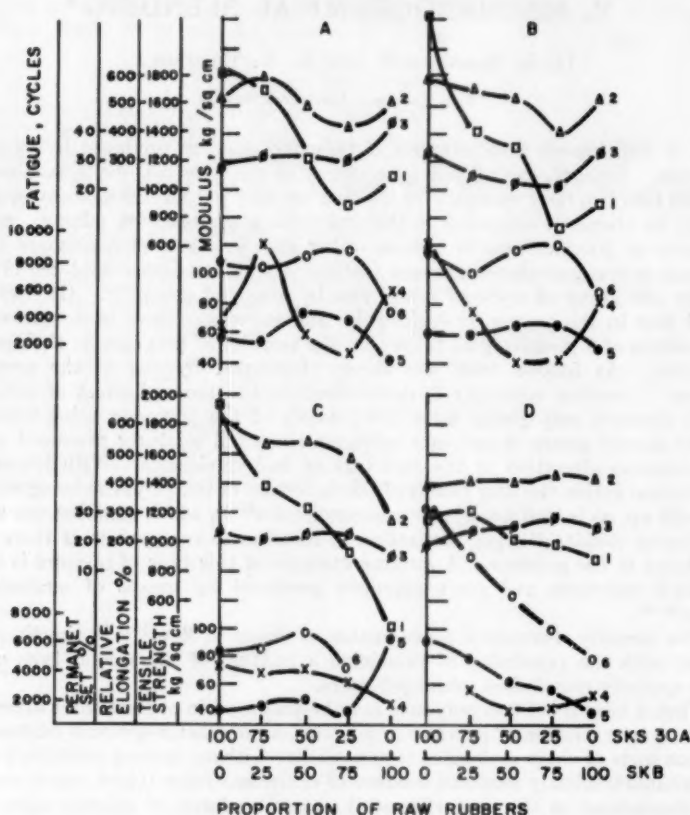
FIG. 1.—Mechanical properties of combined SKS-30A-SKB vulcanizates: A, B—for varying duration of milling on micro rolls, in air (A—mixture prepared 60 min, B—5 min); C, D,—produced by various methods on a special 'scroll' mill in a nitrogen medium (a—Type I, b—Type II). Notation of curves: 1—tensile strength; 2—relative elongation; 3—permanent set; 4—fatigue; 5—200% modulus; 6—300% modulus.

The raw rubbers were processed on micro rolls (180 × 146 mm, friction ratio 1:1.11), on refiner rolls (405 × 146 mm, friction ratio 1:1.22), and also on a special mill for polymers (the scroll type) previously described[24]. The metal parts of the apparatus working on the polymer were cooled intensively with cold water. If this mill was used the raw rubber being processed was either in air or else in nitrogen specially freed from oxygen.

Under such conditions we prepared mixtures of the raw rubbers in various proportions, and also corresponding raw vulcanizing stocks. The processing

time was varied from 5 to 6 min. The resulting mixtures of raw rubbers were dissolved and the behavior of these solutions studied; also, for comparison, the behavior of mixtures of solutions of these rubbers.

The combined vulcanizing stocks were compared by two methods: we either added the necessary compounding ingredients to the original raw rubbers and combined the raw vulcanizing stocks thus produced (Type I) or we added the appropriate compounding ingredients to an already produced mixture of raw rubbers (Type II).

On the finished vulcanizates we determined by standard mechanical methods the tensile strength, relative elongation and permanent set, the 200% and 300% moduli (i.e., the stresses for stretching deformations of 200% and 300% and the fatigue strength under repeated stretching deformation (maximum deformation 100% at a frequency of 250 c/min at room temperature)).

RESULTS

As we might expect, the dependence of the mechanical properties upon composition for the systems SKB with SKS-30A and for SKB with SKS-30 is completely analogous, as may be seen from the comparison of Figure 1b, with the corresponding Figure in a previous paper[1]. In Figure 1a, we show the same dependences for vulcanized rubbers prepared from the same stock subjected to considerably more prolonged milling during mixing.

As we may see from the figure (curves Figure 1a,b) the maxima and minima as they are placed with a 1:3 proportion of SKS-30A and SKB hold good also for longer milling times.

Here again we must note that mixtures of 5% solutions of these rubbers in benzene (and also in benzine) separate into two phases. Thus the behavior of raw SKS-30A rubber does not differ from the behavior of raw SKS-30 rubber, and all the conclusions drawn in references 1–4 in respect of the mutual solubility of SKS-30 and SKB are true also for the systems SKS-30A and SKB.

Since there might be a risk of the inhibiting influence of impurities existing in ordinary commercial rubbers, we carried out analogous experiments with somewhat purer rubber, and particularly with SKS-30A which had not undergone prior thermoplasticization and with SKB without anti-agers and stabilizers.

The investigations led to the conclusion that the general character of the dependences of the properties of such rubbers is maintained in its main features, but on the graphs we observe a slight alteration in the positions of the maxima and minima, and also a certain smoothing out of them (particularly with more prolonged and heavier mechanical action, for instance on refiner rolls).

In this connection it was of interest to experiment with the mixing of these same rubbers under still more severe conditions of mechanical treatment and in the absence of oxygen free to interact actively with free hydrocarbon radicals. This was effected on the scroll type mill, in an atmosphere of pure nitrogen. The results shown in the figure, graphs c and d, for vulcanizates from Type I and II mixes clearly show a considerable reduction in the anomalies in the dependences of the mechanical properties upon composition. The graphs for these dependences have a much flatter character.

It must be noted that the processing of commercial raw SKS-30A and SKB rubbers under the same heavier conditions and in the absence of oxygen does not eliminate the characteristic maxima and minima on the graphs of the dependences of the properties upon composition.

ASSESSMENT OF RESULTS

The data presented above show that microheterogeneous mixtures of polymers produced in the joint processing of raw SKS-30A and SKB rubbers may under definite conditions be homogenized.   These latter lead on the one hand to reinforcing the magnitude and duration of the mechanical action, and on the other to elimination of the possibility of inhibition of free radicals.   The latter condition requires very pure raw rubbers and isolation of the mixture from oxygen contained either in the surrounding air or in the mixture itself (in a dissolved or occluded state).   Unfortunately very pure rubbers, free from stabilizers, antioxidants and antifatigue agents are chemically unstable and thus have an undetermined initial structure.   For just this reason we used systems which were not purified to the ultimate.

Nevertheless the results obtained are in our opinion of fundamental interest. They demonstrate that even a reduction in the content of inhibiting impurities has a perceptible influence upon the character of mixtures formed in the joint processing of these two mutually insoluble polymers.   It follows from this that the processes of mixing of two polymers involves processes in which there occurs not only a mixing up of the chain molecules but also their mechanical scission with the formation of free radicals, interacting among themselves.   The number of acts of scission of chain molecules, naturally, depends upon the intensity of the mechanical action, while the number of acts of combination of radicals may vary sharply as a function of the purity of the polymers which are mixed.   In short, the processes of mixing of the polymers and the mechanical processes of production of block copolymers have a common origin.   The difference is that in mixing polymers on the mill or by means of other mixers the intensity of the mechanical action is less, while the inhibiting role of the oxygen in the air and of other admixtures is greater than in the case of mechanochemical block copolymerization, in which we use special methods of heavy mechanical treatment in the absence of oxygen and with the use of pure polymers.

These ideas are confirmed also by the investigation of the behavior of solutions of the resulting mixtures of raw rubbers.   In all cases where the dependences (property-composition) revealed anomalies (presence of maxima or minima) the corresponding solutions separate into two phases.   In the cases shown in the figure (c, d), where the anomalies in the properties are revealed weakly, the solutions do not separate into phases, while a considerable portion of the mixture generally proves insoluble.   The last circumstance excludes the assumption of improved ordinary mixing in these cases and indicates a profound chemical alteration in the structure of the actual molecules of the mixed polymers.

CONCLUSIONS

1. In the mixing of two polymers with intermixing of molecules, which, depending on the mutual solubility or insolubility, may lead to homogeneous or to microheterogeneous systems, there takes place also a mechanochemical mixing consisting of the formation of graft and block copolymers.

2. The proportion of these processes of mixing is determined by the intensity of and duration of the mechanical action in the process of mixing, and also by the concentration of additives capable of inhibiting the free radicals formed in the mixing.   Of particular importance are special stabilizers, antioxidants and other such additives to the raw rubbers, and also oxygen.

3. The anomalies previously observed in the dependences of the mechanical properties of the vulcanized rubbers based on a combination of two mutually insoluble raw rubbers may be reduced by increasing the part played by the mechanochemical mixing. This opens up ways of producing high quality mixtures of mutually insoluble polymers.

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ELECTRON PARAMAGNETIC RESONANCE OF RADICALS FORMED DURING MILLING *

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It is well known that during the mechanical degradation of polymers there takes place scission of molecular chains and the formation of macroradicals. It is of considerable interest to study the electron paramagnetic resonance (EPR) spectra of the macroradicals produced by milling, and to compare them with the spectra of the macroradicals formed in the process of polymerization, and also during the irradiation of polymers by gamma rays and neutrons. We may endeavor to compare the amount of macroradicals formed with the extent of mechanical destruction (for instance with the area of the new interface which is formed). In addition, as was found by experience, the macroradicals formed by mechanical scission are good models for the investigation of reactivity since practically all of them are in the newly formed surface layers and are therefore very accessible to various chemical influences. They enter easily into reaction with various agents present in the medium since in this process diffusion from the surface is found in practice not to be a predominating factor.

In the present communication we give the first EPR results obtained on mechanically degraded polymers.

EXPERIMENTAL PROCEDURE

We investigated a series of polymers: polymethyl methacrylate, polystyrene, polytetrafluoroethylene, polyisoprene, polyisobutylene, polyethylene and polycaprolactam. The mechanical degradation was effected by milling the polymers with a conical bit in a specially made hermetically-sealed manipulator which could be evacuated to a pressure of 10^{-3} to 10^{-4} mm of mercury. If so desired the manipulator could be filled with liquid nitrogen (containing up to 10% of liquid oxygen) and the polymer milled under liquid nitrogen. The turnings produced in the degradation of the polymer were packed within this sealed manipulator into a quartz ampoule of standard type (3 mm in diameter, 50 mm in length), which could be inserted in the volumetric resonator of the EPR spectrometer or placed in the resonator in a special envelope of polystyrene foam, filled with liquid nitrogen.

Thus it was possible to carry out all the operations, beginning with the degradation of the polymer and finishing with the recording of the spectrum, keeping the polymer turning continuously under the level of the liquid nitrogen or in a vacuum or, finally, bringing it into contact with a gas of any desired composition. The fundamental layout of the EPR spectrometer used by us is described in References (1) and (2).

In the majority of the polymers investigated by us, subjected to degradation at 77° K, and also for certain of them investigated at room temperature *in vacuo*, we observed electron paramagnetic resonance absorption associated with the occurrence of free radicals formed as a result of scission of the molecular chains.

RESULTS

Polymethyl methacrylate (PMMA).—The spectrum of PMMA degraded under a surface of liquid nitrogen has a complex character (Figure 1a) associated with the presence of at least two types of radicals. One of these (I)
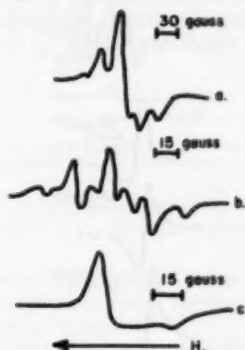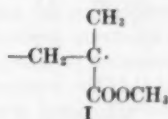

Fig. 1.—Spectrum of PMMA after mechanical degradation; a—in liquid nitrogen; b—*in vacuo*; c—after letting in air.

has a spectrum consiting of 5 lines with spacing of $\simeq 25$ gauss and g factor close to 2, and exhibiting the phenomenon of saturation at a power of the order of 50 mW in the super high-frequency generator. It may be identified with the

$$-CH_2-\overset{\overset{\displaystyle CH_2}{|}}{\underset{\underset{\displaystyle I}{|}}{\underset{\displaystyle COOCH_3}{|}}}C\cdot$$

radical whose spectrum is well known[2-5] from investigations of the polymerization of the monomer, and also of irradiated polymers.

The second radical (II) has a spectrum consisting of one asymmetric line of width $\simeq 22$ gauss, not exhibiting saturation. On raising the temperature to room temperature in the presence of air the spectrum of I disappears instantaneously, while line II disappears only gradually (over 40 min the intensity of the spectrum decreases by e times). It may be supposed that the Radical II is a peroxide radical, occurring as a result of the attachment of a molecule of oxygen (dissolved in considerable amounts in the liquid nitrogen) to a primary hydrocarbon radical. Asymmetric lines of similar type were observed previously during the irradiation of polymers in the presence of air[6, 7].

The suppositions indicated were verified by degradation of PMMA at room temperature *in vacuo*. We observed the characteristic spectrum of Radical I (Figure 1b, in which there is visible a trace of a faint line of Radical II). This

spectrum can exist *in vacuo* over a period of hours, slowly decreasing. On raising the pressure of the air to 0.1 mm mercury the spectrum of I disappeared quite rapidly (5 min), while line II simultaneously became stronger; finally there was established only an asymmetrical line belonging to Radical II (Figure 1b) which then continued to exist over several decades of minutes independently of the presence or absence of air in the system. This picture comprises in the first phase the conversion of the radical with an active center on the carbon (Radical I with characteristic ultrafine structure of the spectrum) into a peroxide radical (Radical II, with structureless spectrum).

Then the peroxide radical slowly decays, evidently by recombination on the surface of the turnings. As we have already indicated[2], the process of recombination of macroradicals depends greatly on the temperature. In the neighborhood of the vitrification temperature (110° C) the macroradicals recombine immeasurably more rapidly.
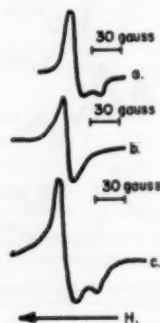

FIG. 2.—Spectra of polymers after mechanical degradation in liquid nitrogen; a—polystyrene; b—polytetrafluoroethylene; c—polyisoprene.

It is interesting to note that in the spectrum of Radical I which is produced during degradation in liquid nitrogen, we did not observe the four intermediate faint lines clearly visible in the spectrum produced during degradation at room temperature. (The same phenomenon occurred also in irradiated PMMA[5].)

From other work[2] it followed that the intermediate lines belong to a macroradical formed as a result of an additional process of transfer of a reaction center from Radical I to the ring groups. At low temperature this transfer does not take place. No additional spectrum, which could be ascribed to the Radical III, which is inevitably formed during the scission of the polymer

$$\begin{array}{c} CH_3 \\ | \\ -C-CH_2 \cdot \\ | \\ COOCH_3 \\ III \end{array}$$
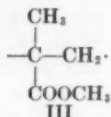
chains, was observed at any time. Apparently this radical is sufficiently active even at 77° K to react with oxygen, with the polymer, or with traces of monomer which have been converted into the more stable Radicals I or II.

Polystyrene, polytetrafluoroethylene, polyisoprene.—In polystyrene, polytetrafluoroethylene and polyisoprene (natural rubber) we observe with deg-

radation under liquid nitrogen a spectrum consisting of one line which does not exhibit saturation and disappears only slowly at room temperature (Figures 2 a, b, c). In the case of polystyrene and polyisoprene this line, as with the peroxide radical of PMMA, is asymmetrical and has clear indications of fine structure. Essentially this fine structure is composed of two poorly resolved spectrum lines. In all three cases, apparently, we observe only the spectra of secondary peroxide radicals of the R—O—O· type. The same kind of spectrum is observed with the destruction of polystyrene at room temperature *in vacuo*. It
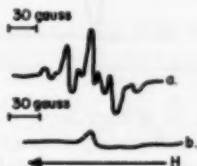

Fig. 3.—Spectra of PMMA after degradation *in vacuo*; a—at 0.5 mW from the super-high-frequency generator; b—the same spectrum at 50 mW.

is possible that as a result of their great activity in relation to oxygen the macroradicals of polystyrene are able to react with the residues of oxygen present in the system.

The asymmetrical nature of the spectra of the peroxide radicals is caused, as is usual in such cases, by the simultaneous presence of radicals of at least two types or by anisotropy of the g factor.

The superimposition of two lines with somewhat different g factors and widths may lead to an asymmetric spectrum and to the appearance of a thin structure on one side of the absorption band. Such a structure is clearly ex-
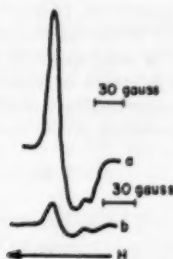
Fig. 4.—Alteration in the spectrum of the peroxide radical with time. Spectrum b was taken 70 min later than a.

pressed in the spectra of the peroxide radicals of polystyrene, PMMA and polyisoprene. The presence of two types of peroxide radicals is easily explained if we bear in mind that in the scission of polymeric chains there are formed two radicals R· and R'·, which, reacting with O_2, can give two peroxide radicals with somewhat different spectra.

The absence of saturation at levels of power of the order of tens of milliwatts in the super high-frequency generator in the absorption bands of the peroxide radicals, and the marked saturation with an associated reduction in the intensity of the spectrum for the majority of the hydrocarbon radicals investigated offers the possibility of separating the spectra where two types of radicals are

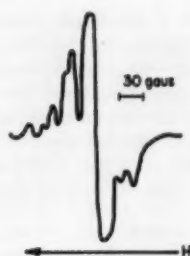FIG. 5.—Spectrum of polyisobutylene after degradation in liquid nitrogen.

present simultaneously, since at a high level of power the spectrum of the hydrocarbon radical is almost completely extinguished (Figure 3).

Finally there are straightforward experimental facts to point to the correctness of our explanation of the asymmetric structure of the absorption band of the peroxide radical. The fact that in the system there are present in fact two different radicals ROO· and R'OO·, having different activity, makes it possible to detect the different kinetics of disappearance of the two components. In Figure 4 we show the spectra of the peroxide radical of PMMA at different times. We are satisfied that the absorption band consists of at least two bands close to each other, one of them disappearing somewhat more rapidly than the other.

In the case of tetrafluoroethylene, which is slightly branched and on scission of the chains gives for the most part two identical radicals $R-CF_2\cdot$, the spectrum of the secondary peroxide radicals studied by us is almost symmetrical.

Polyisobutylene.—Polyisobutylene, after degradation in liquid nitrogen, gives a complex asymmetrical spectrum (Figure 5) associated with the simultaneous presence of radicals both of the hydrocarbon and of the peroxide type.

The spectrum of the latter is analogous to the spectrum of the peroxide radical of polyisoprene. If we subtract it, there remains a spectrum of seven principal equidistant lines with intermediate weaker lines. The seven principal lines may be ascribed to the spectrum of the radical

$$-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\cdot$$
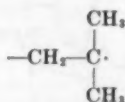
formed with the scission of a chain where the elctron interacts with six protons equivalent in their position relative to the π-electron cloud of an untwinned electron. Two other protons may interact with the electron much more
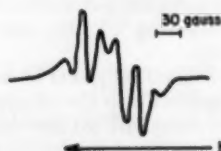

FIG. 6.—Spectrum of polyethylene after degradation in liquid nitrogen.

weakly for the same purely geometrical reasons which were considered in detail in connection with the spectrum of PMMA[4, 5].

Low pressure polyethylene.—Polyethylene gives on degrdation in liquid nitrogen the spectrum shown in Figure 6, having little in common with the spectrum of irradiated polyethylene[6]. It consists of six not fully resolved lines exhibiting saturation; we may ascribe them to the radical formed with the scission of the principal chain at its weakest point—the place of branching of the

$$-CH_2-\overset{\cdot}{C}H-CH_2-$$
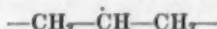
chain, the electron interacting identically with the five neighboring protons. On this spectrum there is superimposed a comparatively weak line not exhibiting saturation, which we may ascribe to the peroxide radical.

Polycaprolactam.—Immediately after degradation of the polymer in liquid nitrogen we may observe weak absorption (Figure 7), which disappears after 1
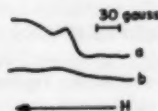

FIG. 7.—Spectrum of polycaprolactam; a—immediately after degradation in liquid nitrogen; b—after 2 min later.

to 2 min at 77° K. Apparently the radicals formed are sufficiently active and mobile to recombine even at such low temperatures. When precautions were taken against oxygen, it was possible to obtain a spectrum of 4 poorly resolved lines.

DISCUSSION

If we carry out degradation of polymers under ordinary conditions, we are far from being able to detect radicals in all cases. The reason for this is clear. Above the glass point the mobility of the macroradicals is sufficiently great so that they disappear immediately by recombination or by disproportionation.

In methyl methacrylate and styrene it was possible to detect considerable concentrations of macroradicals (up to 10^{17} spins/g) with mechanical degradation *in vacuo*. This was not found possible in polyethylene and polycaprolactam.

Under liquid nitrogen the degradation of polymers in practice always leads to the formation of radicals. The amounts of radicals observed in our experiments differ and depend very clearly upon the activity of the radicals. The most stable radicals in our experiments were those of polymethyl methacrylate and polyisobutylene. We observe concentrations of these radicals of the order of 10^{17} spins/g, and they lasted for an unlimited time at 77° K.

The most active were the radicals produced by the degradation of polycaprolactam. Their concentration was of the order of 10^{15} spins/g, and they decayed in 1 to 2 min at 77° K.

As the liquid nitrogen used by us contained a considerable amount of oxygen (up to 10%) we were not able to follow the reaction of addition of the molecules of O_2 to the hydrocarbon radicals to form peroxy radicals.

In spite of the low temperature at which the radicals were formed, the reaction of oxidation sometimes ran to completion. Thus in the case of polyisoprene, polytetrafluoroethylene and polystyrene we were not able to observe

any radicals other than peroxy radicals. On the other hand, the radicals of polymethyl methacrylate, polyisobutylene and polyethylene proved considerably more stable to oxidation at low temperature, and their spectra were studied. In the future experiments will be conducted under liquid nitrogen with oxygen removed.

Judging from the exceptionally high reaction capacity of the radicals produced by mechanical degradation of polymers, the greater part of them are present in the surface layer and are able to take part in chemical reactions without a noticeable diffusion time. It is therefore reasonable to relate the numbers of radicals formed in mechanical degradation to the magnitude of the new surface formed. A calculation of the surface of the turnings for polymethyl methacrylate gives 10^2 to 10^3 sq cm/g. The number of radicals, as already stated, reaches 10^{17} spins/g. Consequently the area for each radical in the surface monomolecular layer will be $\simeq 30$ A^2. This figure agrees satisfactorily with the cross-section of the polymer chain known from X-ray work.

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A STUDY OF MACRORADICALS IN PROCESSES OF POLYMERIZATION AND DEGRADATION. I *

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The concentration of free radicals in reactions in the liquid phase has the order of 10^{-5} mole/l even in such a comparatively favorable case as in the radical polymerization of vinyl monomers. Such a concentration is situated within the limit of the possibilities of modern electronic paramagnetic resonance spectrometers, even if the spectrum of the radicals studied has a small width (of the order of gausses) and paramagnetic saturation is absent at an energy density of the ultrahigh-frequency field of the order of 0.001 erg/cm³. In reactions in a medium with high viscosity, for example in block polymerization, the lifetime of the free radicals, especially of the polymeric ones, increases, and one can depend on a successful application of the method of electronic paramagnetic resonance for investigation of such important reactions as polymerization in its final stages, vulcanization, etc.

The present research is devoted to the use of the method of electronic paramagnetic resonance (EPR) for the study of the polymerization reaction of methyl methacrylate.

EXPERIMENTAL PROCEDURE

The measurements of the paramagnetic spectra were made on the spectrometer whose general features were described previously[1].

In the setup we used a passage resonator of type H_{011}, and as detector a platinum bolometer in connection with a resonance amplifier and a phase-sensitive detector. The magnetic field of the electromagnet was stabilized with an accuracy to 10^{-5} with the aid of an electronic current stabilizer. The spectrum was recorded with the aid of self-recorder EPP-09.

The scheme of automatic tuning of the klystron generator used was similar to that described by Veselago and Irisova[2]. In the set-up we used a low-inertia scheme of thermostatic control of the samples investigated; its arrangement is shown in Figure 1. Along the axis of the resonator is placed a teflon tube with an external diameter of 7 mm and a wall thickness of 0.5 mm, in the center of which is inserted a quartz ampoule with the sample to be investigated. In the clearance between the ampoule and the tube, one blows through, at a sufficient velocity, air warmed with the aid of a Nichrome spiral to the assigned temperature. The temperature-transmitting device is a Chromel-Copel thermocouple, but the continuous regulation of the heating is done with the aid of an arrangement consisting of a reconstructed automatic electronic potentiometer EPV-01 and an electronic-magnetic amplifier. This arrangement permits one to keep the temperature within the interval from 30 to 250° with an accuracy to ± 2°.

For diminution of the vibrations of the resonator arising because of the induction in its walls of induction currents of frequency modulation of the

magnetic field, which limit the admissible amplitude of modulation, the resonator is built up from brass plates 4 mm in thickness insulated from each other by thin leaflets of mica.

The natural quality of such a resonator is about 10,000. The maximum sensitiveness of the spectrometer with such a resonator with a constant time of 30 sec is equal to 3.5×10^{-13} mole of crystalline diphenylpicrylhydrazyl (DPPH).

For determination of the sensitiveness of the spectrometer according to crystalline DPPH it is essential to prepare small enough samples (of the order of 10^{-11} to 10^{-12} mole). In the preparation of mixtures containing such amounts
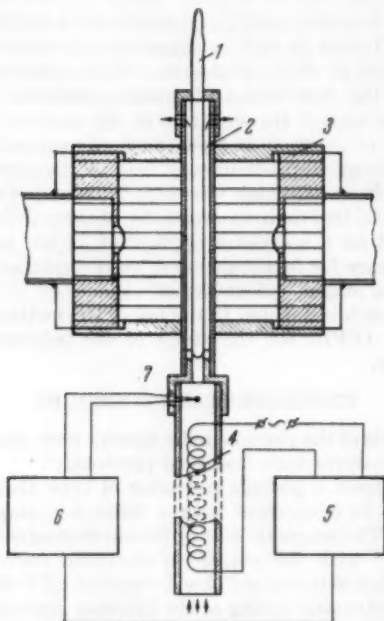

FIG. 1.—Arrangement of the resonator and scheme of temperature control of the sample. *1.* Quartz ampoule; *2.* Teflon tube; *3.* Resonator; *4.* Nichrome spiral; *5.* Electronic-magnetic amplifier; *6.* Automatic potentiometer EPV-01; *7.* Thermocouple.

of DPPH the latter is partially destroyed. Furthermore, different samples display a different width of the spectral lines. It is more correct to calibrate according to a solution of DPPH, although in this case an error may occur because of the influence on the DPPH of oxygen, light, and various impurities in the solvent. We therefore used for determination of the sensitiveness the following method: by successive dilution in benzene of the initial solution with a concentration of 1 mg/ml we prepared samples of different concentrations and took their spectra. In Figure 2 is shown the dependence of the signal of the paramagnetic absorption (U) on the amount of DPPH (μ).

One sees that the proportionality between U and μ is retained down to very small amounts (about 10^{-10} mole). Consequently, it is appropriate to take the spectrum of a relatively large amount of crystalline DPPH, with diminished
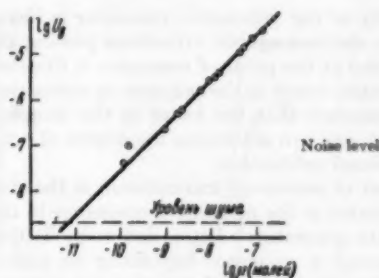
Fig. 2.—Calibration of the spectrometer. Ord.: ln U_0; abs.: ln μ (in moles).

sensitiveness of the amplifier, and to extrapolate the signal obtained to the maximal sensitiveness determined by the "noise" of the setup.

In practice the spectrum was taken with an amount of DPPH equal to 10^{-8} mole. The noise of the apparatus was then recorded and the maximum sensitiveness was calculated (namely, that amount of DPPH which gives the same signal of paramagnetic absorption according to the magnitude of the noise level). In Figure 3 is shown the spectrum of a sample containing 1.1×10^{-10} mole of DPPH dissolved in benzene. The spectrum was taken with a constant time of 4 sec with the resonator described above. The calibration carried out with a resonator having a quality $Q_0 = 22,000$ gives the values of the maximal sensitiveness as 2×10^{-13} mole of DPPH.

RESULTS OF THE EXPERIMENTS AND THEIR DISCUSSION

MEASUREMENT OF THE KINETICS OF POLYMERIZATION
ACCORDING TO THE DIELECTRIC LOSSES

One of the difficult problems in the study of the kinetics of polymerization with medium and high degrees of polymerization is the measurement of the conversion.

The ordinary dilatometric method is inapplicable here because of the high viscosity of the system. In the case of the polymerization of methyl methacrylate we used the method of measurement of the dielectric losses, which is very convenient for this purpose. A quartz ampoule with the system to be polymerized was placed inside a volumetric resonator adjusted to the wave length 3.2 cm, which was excited with the aid of a standard generator. The intensity of the electromagnetic field in the resonator was recorded with the aid of a detector crystal loosely connected with the resonator, in connection with a galvanometer.

In proportion to the polymerization the dielectric losses in the sample decrease, since the angle of loss of polymethyl methacrylate at ultrahigh frequencies is two orders lower than the angle of loss in the monomer. Because

Fig. 3.—Spectrum of 1.1×10^{-10} mole of DPPH dissolved in benzene.

of this the quality of the volumetric resonator is increased, and consequently the power of the electromagnetic vibrations passing through the resonator to the detector crystal at the point of resonance is likewise increased. If one disregards the dielectric losses in the polymer in comparison with the losses in the monomer, and assumes that the losses in the sample are proportional to its monomer content, one can determine the degree of polymerization without the aid of any additional calibration.

The coefficient of resonance transmission is the ratio of the power passing through the resonator at the moment of resonance to the power entering it from the direction of the generator. Let us denote by T_0 the resonance coefficient of transmission through a resonator containing an unfilled ampoule, and by T_1 and T_z the coefficients of transmission through a resonator containing respec-
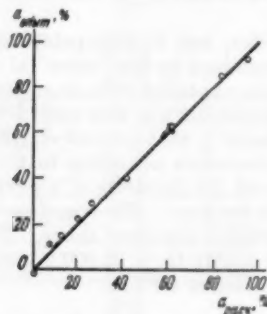

FIG. 4.—Testing the method of determination of the degree of polymerization according to the dielectric losses. Ord.: Experimental per cent; abs.: Calculated per cent.

tively an ampoule with the initial monomer and the same ampoule a certain time after the beginning of the polymerization whose depth of conversion is to be measured. With the aid of the equivalent scheme[3] we obtain the relation

$$a = (1 - \sqrt{T_1/T_z})/(1 - \sqrt{T_1/T_0}) \qquad (1)$$

where a is the degree of polymerization or polymer content in per cent.

To increase the accuracy in the measurement of the coefficient of transmission we always reduced the magnitude of the power falling on the detector crystal to one and the same value by variation, with the aid of a calibrated attenuator, of the power entering from the generator; the accuracy of the method is $\pm 2\text{–}3\%$.

The correctness of the initial assumptions was tested by comparison of the amount of polymer calculated according to Formula (1) with the amount found directly. For this purpose the polymerization was interrupted, the ampoule was broken, and its contents were dissolved in benzene. After the cryosublimation under vacuum the amount of polymer remaining was determined by weighing; the results of the comparison are shown in Figure 4.

MACRORADICALS IN THE POLYMERIZATION PROCESS

The technical monomer was freed from the inhibitor by the usual method and then distilled in vacuum in a quartz ampoule with an internal diameter of
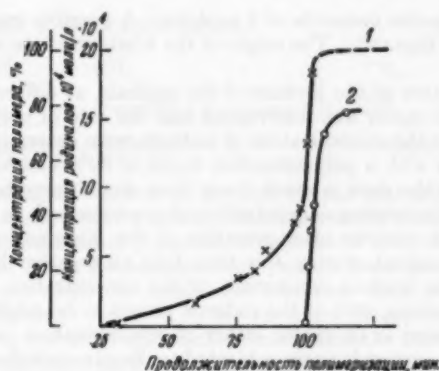
FIG. 5.—Kinetics of the photopolymerization of methyl methacrylate. 1. depth of polymerization; 2. concentration of radicals. Ord.: Concentration of polymer, %, concentration of radicals, 10^a moles/1; abs.: Duration of polymerization, min.

3 mm.   The photopolymerization of methyl methacrylate was carried out without the resonator at 25° with the aid of the light from mercury lamp PRK-4 passed through a water filter.   In certain cases butyl bromide was used as a sensitizer.   After certain intervals of time the dielectric losses were determined and the paramagnetic-absorption spectrum was recorded.   The typical course of the polymerization as a function of the time and the accumulation of radicals are shown in Figure 5 for the case of unsensitized photopolymerization. The absolute concentration of radicals was determined by double integration of the curves and comparison with the corresponding values obtained in the calibration with the aid of crystalline diphenylpicrylhydrazyl (see above).

The observed spectrum did not differ from the spectrum of the radicals "caught" in the polymer in the polymerization of methyl methacrylate in the precipitator and described by Ingram et al.[4] (Figure 6a).   It consists of 5 principal lines with the interval of about 26 gausses and the ratio of intensities 1:4:6:4:1, which corresponds to equal interaction of the unpaired electron

FIG. 6.—Electronic paramagnetic spectrum of the "caught" macroradicals and its change on heating; a, original spectrum; b, c, d, spectrum at successive intervals of time; c is the upper spectrum at the extreme right, d is the lower spectrum at the extreme right.

spin with the magnetic moments of 4 protons.   A possible explanation of this fact was given by Ingram[4].   The origin of the 4 intermediate weak lines is still unexplained.

For determination of the lifetime of the radicals, at different stages of the polymerization the latter was interrupted and the rate of polymerization and rate of decrease of the concentration of radicals were determined in the dark. It was shown that with a polymerization depth of 60% and higher the rate of polymerization in the dark is much lower than would have been expected by proceeding from the existing concentration of macroradicals in the system, and falls to zero a few minutes after cessation of the illumination, although the concentration of radicals during this time falls all together by 15–20%.   At the same time the marked diminution of the concentration of radicals also ceases.   The remaining part of the radicals proves to be relatively stable and at room temperature is incapable either of recombination or of addition of monomer.   If the system is again subjected to illumination the polymerization again takes place with great velocity.
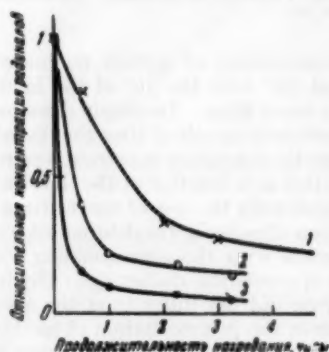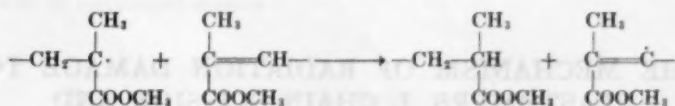

FIG. 7.—Kinetics of the decrease of concentration of the "caught" radicals on heating: *1*. in the polymer obtained without sensitizer at 60°; *2*. the same at 80°; *4*. in the polymer obtained in presence of 1.5% of butyl bromide at 80°.   Ord.: Relative concentration of radicals; abs.: Duration of the heating, hrs.

Thus the spectrum that we observed belonged chiefly to the macroradicals that were caught, whose concentration is connected only indirectly with the kinetics of the polymerization.   It is possible that this stability may be a consequence of the difficult accessibility of the reaction centers of these radicals (the structure of which in all other respects is ordinary) because of their large molecular weight and the convolutions of the chain.

An attempt was made to trace the fate of the caught radicals by heating the polymer.   It was shown that even at 60° the spectrum changes with marked rapidity.   The intensity of the 4 weak intermediate lines of the spectrum increases at the expense of a decrease of the 5 principal ones (Figures 6*b*, *c*, *d*). Finally, the latter disappear completely and there remains a spectrum of the 4 lines with the spacing ~ 26 gausses, which corresponds to the interaction of unpaired electrons with 3 protons.

One of the possible hypotheses is that the caught radical, at high temperature, is able to split off the comparatively weakly bound hydrogen from CH-groups close to the unsaturated ends of the molecules of the polymer, which are

formed as a result of disproportionation:

$$-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\cdot \; + \; \underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}=CH- \longrightarrow -CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{CH}} \; + \; \underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}=\dot{C}-$$

whereupon an unpaired electron in the new radical that is formed, as a result of conjugation, reacts with 3 protons.   Simultaneously with the reorganization of the spectrum, there takes place also a decrease of the total amount of radicals, but at each given temperature only part of them prove to be unstable, while the rest are relatively stable and disappear only with further rise of temperature (Figure 7).   Above T_g the spectrum disappears completely.

An interesting feature of this phenomenon is that the transition from macroradicals of the first kind (with 5 lines) to radicals of the second kind (with 4 lines) is accelerated if low-molecular impurities are present in the polymer, for example residues of the sensitizer (butyl bromide) or traces of oxygen (see Figure 7).   This indicates that the splitting off of hydrogen is realized not directly, as stated above, but by transfer of the reaction center by the low-molecular substances.

In the investigation of the spectrum of radicals of polymethyl methacrylate it was shown that in them saturation sets in even with an energy density of the electromagnetic field in the resonator of the order of 10^{-13} erg/cm^3 (that is, under our conditions, with a power of the ultrahigh-frequency generator of the order of tens of milliwatts).   The time of thermal relaxation T_1 found from this is shown to be of the order of 10^{-5} sec, i.e., unusually large for the case of free radicals (these times ordinarily are of the order of 10^{-8} sec).

To retain the possibility of absolute calibration the paramagnetic spectra in the investigation of the kinetics were recorded with small power levels of the generator (of the order of 1–0.1 milliwatt).

In conclusion we feel obliged to express our thanks to B. L. Erusalimskiĭ for discussion of the results of the work.

CONCLUSIONS

The use of a sensitive electronic paramagentic spectrometer permits one to obtain a number of new quantitative and qualitative data regarding the kinetics of polymerization and behavior of macroradicals with large polymerization depths.   In particular, it is shown that in the photopolymerization of methyl methacrylate in a block of considerable number of sequestered macroradicals accumulates in the final stages.

On the basis of an investigation of the change of the spectra in the heating of the polymer some assumptions are made concerning the secondary reactions of the radicals and concerning the influence of low-molecular impurities on the velocity of these reactions.

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THE MECHANISM OF RADIATION DAMAGE TO ELASTOMERS. I. CHAIN SCISSION AND ANTIRAD ACTION *

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INTRODUCTION

The mechanisms by which high energy radiation affects the properties of elastomers are not completely defined. However, it is accepted that two of the most important secondary events are the crosslinking and scission of polymer chains. These crosslinks and scissions lead to marked changes in polymer properties. Depending on which is predominant, elastomers are either crosslinked with a resulting increase in modulus and decrease in elongation, or undergo scission to a low-modulus, weak material.

Since these property changes are deleterious to most elastomer uses, their prevention is a matter of considerable interest. Born[1] discovered certain substances which have been termed radiation protective agents or antirads. These materials when incorporated into a variety of elastomers served to protect these polymers against the deleterious property changes caused by irradiation.

An essential step in understanding the mechanism by which these antirads are effective is the establishment of (1) whether they prevent scission, crosslinking, or both, (2) whether they act by an antioxidant-like mechanism, or are effective in the absence of oxygen, and (3) whether there are major differences in mechanism from one antirad to the next, or whether they vary only in degree of effectiveness.

The present study was undertaken to obtain more extensive information concerning the effects of antirads upon chain scission induced by high energy gamma radiation. Stress relaxation measurements were chosen as the measure of chain scission.

When a rubber sample is stretched to a given strain and held fixed at this strain, the stress gradually decreases. This phenomenon is termed stress relaxation. At elevated temperatures, this stress decay of sulfur-vulcanized natural rubber approximates an exponential law, as was shown in the pioneering work by Tobolsky and co-workers[2,3]. That this is an oxidative effect can be shown by the three-decade decrease in the rate of stress decay, when oxygen is excluded from the relaxing system. At room remperature the rate of relaxation is much less. A large portion may be due to simple decay of secondary or van der Waals interchain forces.

Recent investigators have shown that the relaxation of sulfur-vulcanized natural rubber at elevated temperatures in air may be adequately represented by the sum of two exponential terms. Le Foll[4] ascribes this to an initial rapid relaxation of secondary interchain forces, followed by a slower oxidative chain scission. Berry[5], on the other hand, has proposed a mechanism whereby the

two exponential terms are related to a relatively slow oxidation of the crosslinks followed by more rapid scission:

$$X + O_2 \xrightarrow{k_1} P$$
$$P \xrightarrow{k_2} \text{scission}$$
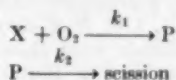
That this mechanism may be operative is borne out by the observations of Bateman and Cunneen[6]. They propose the following mechanism for the oxidation of organic sulfides which they studied:

$$(1)$$

$$(2)$$

$$(3)$$

$$2RS\cdot \longrightarrow RSSR \qquad (4)$$
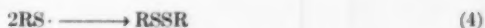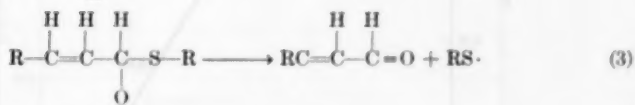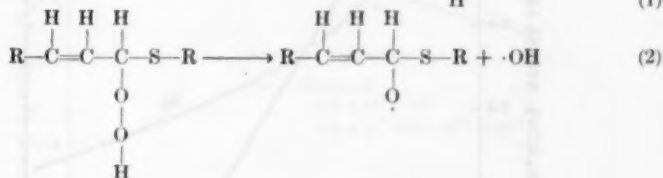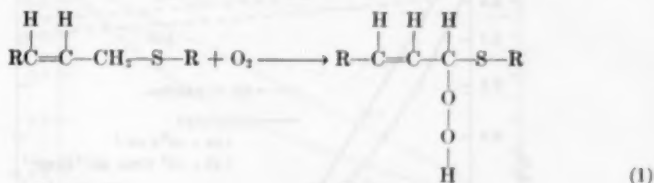
It can be readily seen that step (1) of Bateman and Cunneen's mechanism corresponds to the k_1 process of Berry. Further, Berry's k_2 process involves steps (2), (3), and (4) of Bateman and Cunneen.

EXPERIMENTAL PROCEDURES

As the base recipe of this study, the following ASTM compound was selected[7].

	Parts by weight
Natural rubber	100
Stearic acid	3
Zinc oxide	5
Sulfur	3
Benzothiazolyl disulfide	1
Phenyl-2-naphthylamine	1
EPC carbon black	50

To this control recipe were added five parts of eleven selected antirads: (1) N-phenyl-N'-o-tolylethylenediamine (FLX); (2) N-cyclohexyl-N'-phenyl-p-phenylenediamine (Antiox 4010), (3) 6-phenyl-2,2,4-trimethyl-1,2-dihydro-

quinoline (Santoflex B), (4) N,N'-dioctyl-p-phenylenediamine (UOP-88), (5) 2-naphthylamine, (6) 1,4-naphthoquinone, (7) phenylhydroquinone, (8) 2-naphthol, (9) N,N'-diphenyl-p-phenylenediamine (35%) + phenyl-1-naphthylamine (65%) (Akroflex C), (10) N,N'-dicyclohexyl-p-phenylenediamine, and (11) p-quinone. The antirads were chosen from those either showing maximum antirad effectiveness during Born's empirical study[1] or having structural variations of interest. It is recognized that the solubility limit was
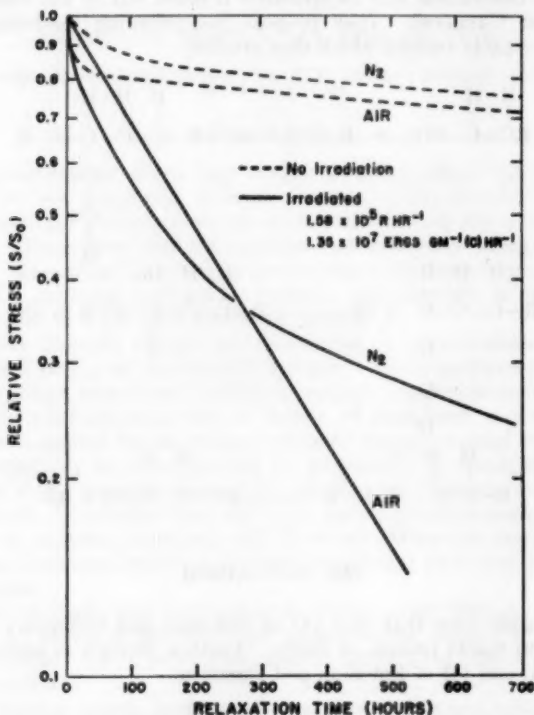

FIG. 1.—The stress relaxation of carbon black-loaded natural rubber containing 1 part phenyl-2-naphthylamine (control).

exceeded for some of these antirads in the rubber. This fact makes comparisons of antirad effectiveness unreliable, but it in no way affects the mechanistic conclusions of this work.

The compounds were mixed as described in standard ASTM procedures. All of the samples were cured to optimum cures as determined by physical properties. The 0.025-in.-thick cured sheets were cut into 1.25-in. × 0.25-in. strips for testing.

Relaxation measurements were made on the Multilaxometer which has been described previously[1]. Experiments were made both in air and in nitrogen, both with and without irradiation. A Co-60 gamma source was used which provided a uniform gamma radiation flux of 1.35×10^7 ergs/g^{-1} (C) hr^{-1} (1.58×10^5 R hr^{-1}).

RESULTS AND DISCUSSION

The types of results which were obtained are shown in Figures 1 and 2. Stress relaxation was plotted as log (S/S_0) vs. t, where S is the stress at time t and S_0 is the stress at $t = 0$. The rates of stress relaxation (k) were then taken directly as the slope of the linear portion of the curves (expressed as hours^{-1}). The rates of relaxation under irradiation have been corrected for the relaxation which would be noted without irradiation by simple subtraction of the rates.
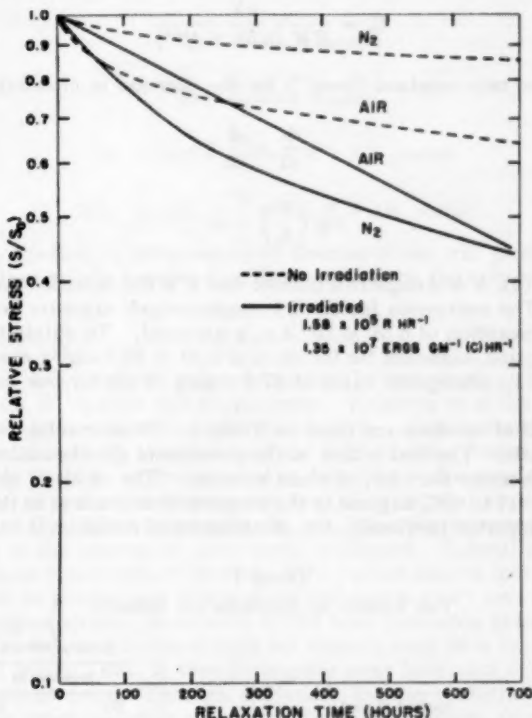

FIG. 2.—The stress relaxation of carbon black-loaded natural rubber containing 5 parts N-cyclohexyl-N'-phenyl-p-phenylenediamine.

It is assumed that the ratio of the stress at fixed elongation of a rubber sample before and after a given continuous stress relaxation is the same as the ratio of load-bearing chains (ν) before and after the same relaxation. If this is true, then the number of load-bearing chains broken or the number of scissions can be calculated directly if the number of load-bearing chains is known initially[5].

Other research work[5] has shown that the effective molecular weight between crosslinks (M_c) for the natural rubber stock employed in these experiments, containing 50 pphr of EPC black, may be represented by the following rela-

tionship:

$$\frac{1}{M_c} = \frac{M_{100}}{73.7 \times 10^4} \tag{1}$$

where M_{100} is the modulus (expressed in psi) at 100% elongation.

If the original molecular weight between crosslinks is known, and it is noted that the number of crosslinks per gram is given by N/M_c, the number of scissions per 100 e.v. energy absorption (G_s) may be readily determined:

$$G_s = \frac{kN}{RM_c(6.58 \times 10^{17})} \tag{2}$$

where k is the rate constant (hour^{-1}) for the decrease in crosslinks described earlier.

$$-\frac{ds}{dt} = \frac{d}{dt} k \tag{3}$$

$$\log\left(\frac{S}{S_0}\right) = kt \tag{4}$$

In Equation (2), N is Avogadro's number and R is the radiation dose in megaroentgens. The conversion factor of 1 megaroentgen exposure being equivalent to the absorption of 6.58×10^{19} e.v./g was used. To obtain this value, a weight absorption coefficient for the stock of 2.89×10^{-2} cm^2/g was calculated, and the new air absorption value of 87.7 ergs/g of air for one roentgen was assumed[10].

The yields of scissions are listed in Table I. These results reveal several interesting facts. The first is that in the presence of air, the antirads serve in all cases to decrease the yield of chain scission. The yields of chain scission in air are only 11 to 60% as great in the presence of antirads as in their absence. As has been reported previously, the effectiveness of radiation in causing chain
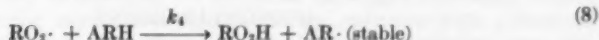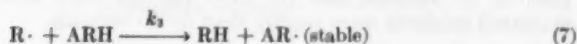
TABLE I

THE EFFECT OF ANTIRADS ON SCISSION

| | G (events/100 e.v.) | |
| | Scissions in | |
Antirad (5 phr)	N_2	Air
None (1 phr phenyl-2-naphthylamine)	2.7	13
N-Phenyl-N'-o-tolylethylenediamine	1.8	4.3
N-Cyclohexyl-N'-phenyl-p-phenylene-diamine	1.2	1.4
6-Phenyl-2,2,4-trimethyl-1,2-dihydro-quinoline	1.9	4.2
N,N'-Dioctyl-p-phenylenediamine	1.5	5.0
2-Naphthylamine	1.6	5.6
1,4-Naphthoquinone	2.0	5.6
Phenylhydroquinone	2.2	5.4
2-Naphthol	1.3	4.1
N,N'-Diphenyl-p-phenylenediamine (35%) + phenyl-1-naphthylamine (65%)	1.4	3.7
N,N'-Dicyclohexyl-p-phenylenediamine	1.5	3.0
p-Quinone	2.8	7.8

scission is greatly reduced in the absence of air. This is true whether antirads are present or not.

The most interesting observation, however, is that the antirads are effective in the absence of air, as well as in its presence. In the absence of air, the yields of chain scission are 45 to 82% as great in the presence of antirads as in their absence. Only in the case of p-quinone is the antirad ineffective in the absence of air.

Qualitatively these observations could be explained by assuming the following mechanisms (ARH = antirad):

$$R \cdot \xrightarrow{k_1} \text{Scission} \tag{5}$$

$$RO_2 \cdot \xrightarrow{k_2} \text{Scission} \tag{6}$$

$$R \cdot + ARH \xrightarrow{k_3} RH + AR \cdot \text{(stable)} \tag{7}$$

$$RO_2 \cdot + ARH \xrightarrow{k_4} RO_2H + AR \cdot \text{(stable)} \tag{8}$$

Irradiation, whether in the presence or absence of air, will yield $R \cdot$ radicals, but in air these will be converted to $RO_2 \cdot$ radicals by the very rapid reaction:

$$R \cdot + O_2 \xrightarrow{k_5} RO_2 \tag{9}$$
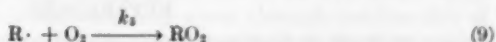
Thus, in air, $RO_2 \cdot$ radicals will predominate in the system, whereas, in the absence of air, $R \cdot$ radicals will predominate. Evidence from the large body of polymer oxidation research indicates that $k_2 > k_1$. Consequently, it would be expected and is actually observed that the yield of chain scission is less in the absence of air than in its presence. Any reactions of the type (7) or (8) will decrease the radical concentration and thus the rate of chain scission by reactions (5) to (6). If we assume that $k_4 > k_3$, then the decreased effectiveness of antirads in the absence of air is easily explained. Indeed, evidence from other reactions would indicate that the $RO_2 \cdot$ radical may be more energetic.

It should be pointed out that in stress relaxation, every load-bearing chain which undergoes scission contributes to the total relaxation unless the broken chain radical ends reunite before they can migrate away from each other under the applied stress. But, if they do migrate away from each other, they may undergo various fates. Through oxidation, hydrogen abstraction, reaction with various other materials present, or disproportionation, these free radical ends may be stabilized in a permanent or nontransient broken form. On the other hand, by combination with other free radical ends or addition to unsaturated sites present in the polymer matrix, the free radical ends may reunite with main chains and essentially disappear. Thus the chain scissions measured by stress relaxation may be both transient and nontransient in nature. Yields of chain scission measured in this way may be considerably larger than those measured by rates of gel formation or related techniques, since these latter methods measure only the nontransient chain scissions.

CONCLUSIONS

The effect of antirads on chain scission as measured by stress relaxation is one of inhibition both in the presence of air and to a lesser extent in its absence.

This can be explained by assuming a reactivity of the antirads with RO_2·
radicals yielding stable products, and a somewhat decreased reactivity with R·
radicals.   A greater tendency of RO_2· radicals to lead to chain scission than R·
radicals seems to be indicated.

SYNOPSIS

The effect of antirads on the gamma radiation yields of scission in black
loaded natural rubber stocks has been studied.   The yield of chain scission
has been measured by stress relaxation methods.   The antirads were found to
decrease the rate of chain scission, both in air and under nitrogen, with the
antirad effectiveness being greater in the former case.   The presence of oxygen
accelerated the radiation induced chain scission.   These results may be ex-
plained if it is assumed that (1) RO_2· radicals lead to chain scission more readily
than do R· radicals, and (2) RO_2· radicals react with antirads leading to
stabilized products more readily than do R· radicals.

ACKNOWLEDGMENT

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THE MECHANISM OF RADIATION DAMAGE TO ELASTOMERS. II. CROSSLINKING AND ANTIRAD ACTION *

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INTRODUCTION

Chain scission and crosslinking are the most important secondary events which result from the interaction of high energy radiation with polymers. Chain scission, particularly the effect of antirads on chain scission, was discussed in the first paper of this series[1]. Crosslinking is, however, equally important.

The mechanisms involved in crosslinking are not at all well understood[2]. It has been postulated that crosslinking may occur through combination of polymer radicals or through an addition of polymer radicals to unsaturation present in the polymer molecules. If the former mechanism predominates, the combination of secondary radicals will lead to tetrafunctional crosslinks, while the combination of a primary radical with a secondary radical will lead to a trifunctional crosslink. Similarly, radical addition to unsaturation can cause the formation of either tetra- or trifunctional crosslinks, depending upon the fate of the radical formed as the addition product.

These mechanisms are all merely speculative. Proof of their validity is lacking. The reality of crosslinking of some sort is not subject to doubt, however. It is evidenced by the increases in gel content, increases in modulus, and other similar property changes which polymers undergo during irradiation.

The present study was devoted to the changes in the high energy radiation-induced crosslinking caused by the presence of antirads (chemicals serving to reduce the deleterious property changes of polymers during irradiation). Once again, the major points of interest were (1) whether the antirads prevented crosslinking, (2) whether they were effective in the absence of oxygen or functioned rather, simply as antioxidants, and finally (3) whether the antirads differed only in degree of effectiveness or whether there were major qualitative differences among them.

The rate of development of crosslinks in elastomers containing various antirads was followed as a function of radiation dose. A carbon black-filled natural rubber stock was chosen as the control, since it had been used for the study of polymer scission by radiation and antirad protection against this scission in the preceding study. The antirads were chosen as before, from those showing maximum antirad effectiveness in an empirical study by Born[3] and those having structural variations of interest.

EXPERIMENTAL PROCEDURES

The same recipe was used as that in the study of radiation induced chain scission, expect that the curing ingredients were eliminated:

	Parts by weight
Natural rubber	100
Phenyl-2-naphthylamine	1
EPC carbon black	50

To this control recipe were added five parts of one of the following nine anti-rads: (1) N-phenyl-N'-o-tolylethylenediamine (FLX), (2) N-cyclohexyl-N'-phenyl-p-phenylenediamine (Antiox 4010), (3) 6-phenyl-2,2,4-trimethyl-1,2-dihydroquinoline (Santoflex B), (4) N,N'-dioctyl-p-phenylenediamine (UOP-88), (5) 2-naphthylamine, (6) 1,4-naphthoquinone, (7) phenylhydroquinone, (8) 2-naphthol, and (9) a mixture of 35% N,N'-diphenyl-p-phenylenediamine and 65% phenyl-1-naphthylamine (Akroflex C).

Once again comparisons of antirad effectiveness are not possible, since in some of these compounds the solubility limit of the antirads in the rubber was exceeded. Mechanistic conclusions remain unaffected, however.

All of the materials were added to the rubber on a mill held at a mill roll temperature of 160° F. The mixture was milled for 15 min before being sheeted off. Sheets of 0.025 inch thickness were molded at 212° F for 10 min between cellophane sheets.

Each of the sheets was cut into strips 0.25 inch wide and approximately 1.35 inches long. After removal of cellophane, each of the strips was placed in a small open test tube if the irradiations were to be performed in air. Samples destined for vacuum irradiation were sealed into small glass ampules after being evacuated at a pressure of less than 10^{-6} mm Hg for 16 hr or more. Calculation of the diffusion rate of oxygen through these samples and past experimental evidence have proven this treatment to be adequate, even on a conservative basis, to remove any oxygen effects.

The samples were irradiated in the B. F. Goodrich Gamma Facility. The dose rates varied from 5.2×10^4 to 7.3×10^4 r/hr, and the time to complete the irradiations desired ranged from 6 to 19 days. The dosages were determined by glass slide dosimetry at each sample position[4]. The glass slides were placed in the same holders (test tube or glass capsules) as were the samples in order to compensate for any shielding effect of the holders. The experiments were conducted at room temperature.

The irradiated samples were removed from their holders and their lengths were measured. They were than allowed to swell for 24 hr in benzene containing 0.1% of phenyl-2-naphthylamine. After blotting the samples dry, their swollen length was measured. It had been previously demonstrated that samples treated in this fashion swell isotropically.

The molecular weight between crosslinks M_c was calculated from the equation[6]

$$M_c = \frac{-\rho V_1 [1 - 2(M_c/M)][v_{2m}^{\frac{1}{3}} - (v_{2m}/2)]}{[\ln(1 - v_{2m}) + v_{2m} + \chi v_{2m}^2]}$$

where

$$v_{2m} = \frac{(f\rho_T/\rho)}{[(L/L_0)^3 - 1 + (f\rho_T/\rho)]}$$

and where ρ is the density of the polymer ($= 0.93$), f is the weight fraction polymer in the compounded stock, ρ_T is the density of the compounded stock ($= 1.11$), V_1 is the molar volume of the solvent ($= 89.32$), M is the primary chain molecular weight, χ is the solvent-polymer parameter ($= 0.44$), and L_0 and L are the original and swollen sample lengths, respectively.

The corrective term for end groups $[1 - 2\ (M_c/M)]$ was neglected in this work due to the difficulty in obtaining accurate measurements of M in a carbon black-filled elastomer.   The effect of this correction is not great since in most cases $M_c \ll M$.   No correction was made for any sol which might be present. Previous experience indicated that the amount of sol would be negligible.
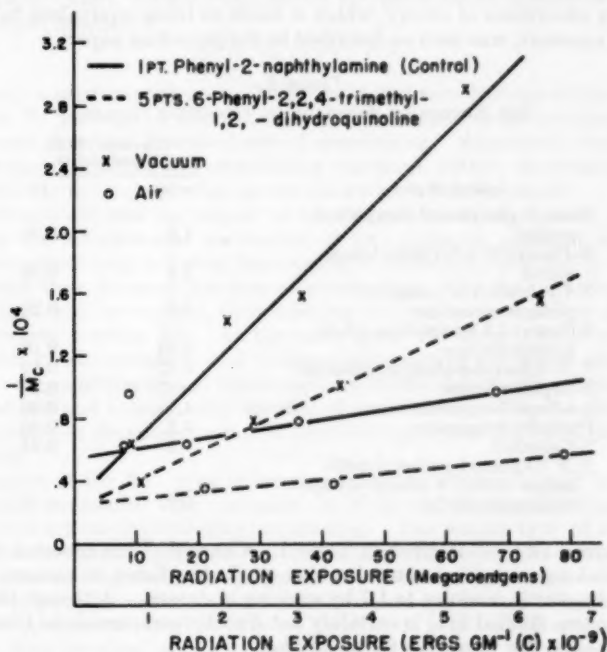
FIG. 1.—Changes in crosslink level during irradiation of carbon black-loaded natural rubber.

As Moore and Watson[6] pointed out in their studies relating to the measurement of crosslink density, the swelling technique gives a measure of all effective crosslinks.   These may include not only the conventional chemical crosslinks, but also effective crosslinks caused by chain entanglement or crosslinks resulting from polymer-filler interactions.

RESULTS AND DISCUSSIONS

The type of results obtained is illustrated in Figure 1, where the reciprocal of the molecular weight between crosslinks is shown as a function of radiation dosage R for the control and the stock containing 6-phenyl-2,2,4-trimethyl-1,2-dihydroquinoline.   The radiation dosage has been expressed both in terms of

megaroentgens exposure and ergs per gram of carbon exposed to the same radiation flux, since a general agreement as to acceptable terminology has not yet been reached.

The slope of the linear portion of these curves was then measured to obtain the rates of crosslinking expressed as the crosslink density change per megaroentgen exposure $[1/M_cR]$. These may be readily converted to crosslink yield G_x by the equation

$$G_x = [(1/M_cR] \, (N/2) \, (6.58 \times 10^{-17})$$

In this equation, N is Avogadro's number. The conversion factor of 6.58×10^{19} e.v./g absorption of energy, which is taken as being equivalent to 1 megaroentgen exposure, was used as described in the preceding paper[1].

TABLE I

THE EFFECT OF ANTIRADS ON CROSSLINK YIELDS

Antirad (5 phr)	G, events/100 ev, (crosslinks) in	
	Vacuum	Air
None (1 phr phenyl-2-naphthyl-amine)	1.9	0.29
N-Phenyl-N'-o-tolylethylenedi-amine	1.1	0.28
N-Cyclohexyl-N'-phenyl-p-phenylenediamine	1.3	0.33
6-Phenyl-2,2,4-trimethyl-1,2-di-hydroquinoline	0.83	0.19
N,N'-Dioctyl-p-phenylenediamine	0.87	0.12
2-Naphthylamine	0.87	0.30
1,4-Naphthoquinone	1.1	0.48
Phenylhydroquinone	1.1	0.46
2-Naphthol	1.1	0.24
N,N'-Diphenyl-p-phenylenedi-amine (35%) + phenyl-1-naph-thylamine (65%)	0.97	0.27

The crosslink yield is given in Table I. Charlesby[7] has reported G values for crosslinking in unfilled natural rubber stocks irradiated in vacuum ranging from 1.1 by elastic modulus to 1.7 by swelling in decane. Although the black-loaded system studied here is certainly not directly comparable to Charlesby's unfilled stocks, the values for G_x are similar.

It is immediately apparent that all of the antirads studied decrease the yield of crosslinks by a factor of approximately two in the absence of oxygen. Electron paramagnetic resonance measurements have proven directly the presence of considerable number of free radicals in polymeric systems during irradiations[8, 9]. Analogy to simple chemical reactions involving free radical dimerization, leads us to presume that crosslinking may occur in the same fashion. However, the ease of free radical addition to olefinic unsaturation means that this must also be considered as a potential crosslinking reaction. In any event, any reaction leading to a decrease in the concentration of free radicals would presumably decrease the rate of crosslinking.

We may postulate that the antirads may react with polymeric free radicals in the following fashion:

$$R\cdot + ARH \longrightarrow RH + AR\cdot \quad \text{(stable)} \tag{1}$$

Here ARH refers to an antirad molecule containing a labile hydrogen. The antirad free radical may stabilize itself by dimerization with a similar radical or by rearrangement mechanisms. This mechanism is supported by recent studies by Shelton[10] of the relative antioxidant properties of conventional antioxidants as compared to those in which deuterium replaced the labile hydrogen atoms. The less labile deuterium gave less oxidation protection than the hydrogen substituted material. Since oxidation is also a free radical process, it seems logical to assume that the labile hydrogen neutralization of the polymeric free radical is also an important step in antirad action.

Irradiation in air with no antirads present resulted in a reduction in crosslinking yield. Here the same number of polymer radicals should be formed, but the rapid reaction

$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad (2)$$
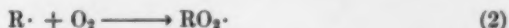
should play a predominant role. This should lead to a decrease in the concentration of $R\cdot$ radicals to a level below that developed in an irradiation in a vacuum and thus to a decreased rate of crosslinking. Apparently the $RO_2\cdot$ is not an active participant in crosslinking reactions; rather, its presence leads predominantly to chain scission, as was shown in our earlier paper[1].

If antirads are now introduced to the oxygen-containing system, we may postulate the simultaneous occurrence of two different types of reactions. First, the antirad may act as in the vacuum to further decrease the $R\cdot$ concentration and thus decrease the rate of crosslinking. On the other hand, the antirad itself may be oxidized, thus reducing the local concentrations of oxygen and inhibiting reaction (2). At the same time, the antirad itself would be inactivated by its oxidation, and consequently reaction (1) would also be decreased. The combination of these reactions would increase the concentration of $R\cdot$ radicals and consequently the rate of crosslinking. Thus, antirads may either increase or decrease the rate of crosslinking, depending on relative rates of reaction.

Examples of the first type of reaction, crosslink inhibition, may be seen in compounds containing the antirads N,N'-dioctyl-p-phenylenediamine or 6-phenyl-2,2,4-trimethyl-1,2-dihydroquinoline. The second type of behavior, crosslink acceleration, is shown by compounds containing the antirads 1,2-naphthoquinone or phenylhydroquinone.

All of these mechanisms are speculative and are quite likely to be too simple to explain these reactions when they are understood in detail. For the present, however, they do stand as one mechanistic explanation for the observed facts.

These observations are qualitatively similar to those of Turner[11] who studied the effect of additives on gum natural rubber, and those of Prober[12] who conducted a similar study on polyethylene.

It is informative to compare the crosslink yields obtained here to the scission yields which we reported earlier[1]. The ratio of G (scission) to G (crosslinking) is shown in Table II. It should be pointed out that the scission yields in the absence of air were determined from measurements at stress relaxation conducted under nitrogen. Other work in this laboratory, however, has demonstrated the equivalence of nitrogen and vacuum environments.

Table II shows that the scission-to-crosslinking ratios range from 45 to 4.3 in air and from 2.3 to 0.92 in vacuum. This may at first seem unusual when it is recalled that Charlesby[13], studying irradiated, unfilled natural rubber, and others studying similar systems, report ratios which are less than 0.1. An essential difference should be stressed, however.

In our earlier paper[1], the point was stressed that stress relaxation measures all chain scissions in which the broken chain ends migrate away from each other under the applied stress before they reunite. We must however consider what happens to these broken chain ends. First of all, they may be tied back into the polymer substrate by combination with other free radical ends or by addition to unsaturated sites along the polymer chains. These we will term transient chain scissions. On the other hand, the broken chain ends may be stabilized by oxidation, hydrogen abstraction, disproportionation, or reaction with various other substances present. These we will term permanent chain scissions. Measurements based on gel formation such as those of Charlesby really measure only permanent chain scission.

TABLE II

THE EFFECT OF ANTIRADS ON THE RATIO OF SCISSION TO
CROSSLINK YIELDS

Antirad (5 phr)	Ratio of G (scission) to G (crosslinking)	
	No air	Air
None (1 phr Phenyl-2-naphthyl-amine)	1.4	45
N-Phenyl-N'-o-tolylethylenedi-amine	1.6	15
N-Cyclohexyl-N'-phenyl-p-phenylenediamine	0.92	4.3
6-Phenyl-2,2,4-trimethyl-1,2-dihydroquinoline	2.3	22
N,N'-Dioctyl-p-phenylenediamine	1.7	42
2-Naphthylamine	1.8	19
1,4-Naphthoquinone	1.8	12
Phenylhydroquinone	2.0	12
2-Naphthol	1.2	17
N,N'-Diphenyl-p-phenylenedi-amine (35%) + phenyl-1-naphthylamine (65%)	1.4	14

The present work, when compared to the work of Charlesby and others, indicates that temporary chain scission is greater than permanent chain scission by a factor of 10 to 100. The vast majority of the stressed chains broken by radiation induced reaction must reunite after relaxation.

CONCLUSIONS

All of the antirads studied serve to decrease the rate of crosslinking of carbon black loaded natural rubber during irradiation in a vacuum. Oxygen also serves very effectively as an antirad toward crosslinking. In air, some antirads enhance this protective effect of oxygen; others serve actually to increase the rate of crosslinking.

Mechanisms sufficient but not necessary to explain these observations are presented. They involve reactions of the antirads with polymer radicals, viz.:

$$R\cdot + ARH \longrightarrow RH + AR\cdot \qquad \text{(stable)}$$
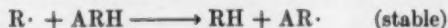
reactions of oxygen with polymer radicals, viz.:

$$R\cdot + O_2 \longrightarrow RO_2\cdot$$

and reactions of oxygen with antirads, viz.:

$$ARH + O_2 \longrightarrow oxidized\ products$$

The ratio of scissions to crosslinks ranges from 45 to 4.3 in air and 2.3 to 0.92 in vacuum. The sol-gel measurements of other workers show, however, that most (90–99%) of these scissions are only temporary chain breaks which are rapidly reformed.

SYNOPSIS

The effect of antirads (compounds added to reduce changes of polymer properties during irradiation) on the crosslink yields in black-loaded natural rubber stocks during gamma irradiation has been measured. The crosslink yields were determined by swelling techniques. Antirads decrease the crosslink yields if oxygen is absent. Oxygen alone effectively decreases crosslink yields. In the presence of oxygen some antirads further decrease crosslink yields, while others increase crosslink yields by their presence. These results may be explained in terms of competitive reactions between R· radicals, the antirad, and oxygen. Evaluation of the ratios of crosslink yields to scission yields indicates that most of the scission is temporary in nature, the chain breaks being reformed rapidly.

ACKNOWLEDGMENT

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INFLUENCE OF ACCELERATOR RESIDUES ON
AGE RESISTANCE OF VULCANIZATES *

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The great dependence of age resistance of elastomeric vulcanizates upon the curing system used in their preparation is a well-recognized phenomenon[1-4]. It has been well established that diene elastomers cured using certain accelerator and peroxide curing agents have superior age resistance, in both "natural" and accelerated aging, over those cured using the more common sulfur-accelerator combinations[5-6].

The reasons for this greater age resistance have been ascribed to various causes, chief among which is the increased stability of the network structures resulting from use of these curing systems[7-8]. The latter conclusion is usually supported by the comparison of bond energies of the carbon-carbon bond at approximately 63 kcal/mole with monosulfide at 55 and polysulfide at 28 kcal/mole. (It is implied that the most age-resistant rubbers are those having a preponderance of the more stable carbon-carbon and monosulfide crosslinks.) But the two observations below are difficult to reconcile with this explanation:

1. The chief manifestations of aging in the diene rubbers are reduced elongation and increased hardness and modulus which result from the *formation* of additional crosslinks rather than rupture of those already present. As a consequence of this, the presence of inherently more stable structures such as the carbon-carbon crosslink may actually lead to poorer age resistance as reflected by physical property changes after aging.

2. Recent studies, the results of which will be furnished later in this paper, have indicated that completely uninhibited peroxide and gamma radiation cured vulcanizates have extremely poor resistance to accelerated aging at 212° F.

Further aging studies on vulcanizates based on the following four curing systems have indicated that only those vulcanizates cured with accelerators (in the absence of elemental sulfur) have excellent age resistance, whether inhibitor has been added or not:

1. Sulfur/accelerator (1.75 parts per hundred rubber hydrocarbon (phr) sulfur plus 1.00 phr N-cyclohexyl-2-benzothiazyl sulfenamide).

2. Accelerators only (1.0 phr dicyclopentamethylene thiuram tetrasulfide (DCPTTS) plus 1.0 part mercaptobenzothiazole (MBT).

3. Peroxide (1.0 phr dicumyl peroxide).

4. Radiation (33 megarads gamma radiation).

Unless otherwise indicated, the above curing combinations will be the ones obtaining throughout this paper.

Since excellent age resistance was obtained with the accelerator cure even in the absence of added inhibitor (antioxidant), these results appear to indicate that this age resistance may be related to the inherent stability of this type of vulcanizate. It is well recognized, however, that certain classes of accelerators provide some antioxidant protection to a vulcanizate[3].

It was the objective of this investigation to attempt to ascertain whether the inhibitor function is dominant in establishing good age resistance or whether such resistance is a prime function of the stability of certain network structures resulting from the use of specific curing systems.

PROCEDURE AND RESULTS

Formulations of rubber compounds used in this study are listed in Table I. These compounds were mill mixed, cured, and tested in accordance with ASTM procedures where applicable. The radiation cures were accomplished in a

TABLE I

COMPOUND FORMULATIONS

Compounding ingredient	Parts by weight	
	SBR compound	Hevea compound
Uninhibited SBR 1500	100	
Pale crepe		100
Zinc oxide	3	5
Stearic acid	2	1
Phenyl-2-naphthylamine (PBNA)		1
Tellurium		0.5
Tetramethylthiuram disulfide (TMTD)		3
MAF (FEF) carbon black	50	50
Curatives	as indicated	
Inhibitor	1 PBNA where indicated	

All test pad cures were for 30 minutes at 307° F except radiation cures which were accomplished by a dose of 33 megarads of gamma radiation.

manner previously described[5]. The bulk of the accelerated aging was done in an air oven at 212° F since previous work had indicated that aging under these conditions could be correlated, at least qualitatively, with "natural" aging. In order to minimize migration of ingredients between compounds during aging, only those vulcanizates having the same inhibition and cure were aged simultaneously.

A sample thickness of 0.040-inch was used throughout since it has been shown[9] that the rate of oxidation may be affected by the rate of diffusion of oxygen into thicker specimens. Since the ultimate elongation varies most regularly with aging and is one of the best indications of the aged condition of SBR vulcanizates, this property was emphasized in the graphical presentation of some of the data. In those cases in which elongation alone is shown, the other properties, such as tensile strength, modulus, and hardness, showed a degree of deterioration in the respective vulcanizates which was comparable to that indicated by elongation changes.

Two principal techniques were utilized in preparing specimens for aging. In the first, dumbbell and National Bureau of Standards (NBS)[10] strain test

specimens of the vulcanizates were acetone extracted (Soxhlet extractor) to remove inhibitors where present, free sulfur, and accelerator residues. In order to establish the efficiency of this extraction and the time required for complete extraction, SBR vulcanizates were prepared using the base recipe shown in Table I except that radioactively tagged PBNA was included. These vulcanizates were acetone extracted, and the counting rate monitored in the extract and in the residual vulcanizate.

The results in Table II indicate that the extraction process was very efficient regardless of the type sample, time employed, and curing system except for the radiation cure in which a significantly lower percentage of inhibitor was recovered. Possible reasons for this condition will be mentioned when the aging of radiation cured SBR is discussed.

TABLE II

% RADIOACTIVE PBNA EXTRACTED FROM CURED AND
UNCURED SBR COMPOUNDS

Cure used	Type sample	Extraction time, hrs.	% extracted
Uncured	thin sheet	24	91.0
Sulfur/accelerator	dumbbell	24	92.6
Sulfur/accelerator	dumbbell	48	92.5
Sulfur/accelerator	finely shredded	24	94.6
Sulfur/accelerator	finely shredded	48	94.7
Peroxide	finely shredded	24	91.4
Peroxide	dumbbell	24	91.0
Radiation	dumbbell	24	78.2
Sulfur/accelerator	dumbbell	6	91.3

In the second technique, small quantities of ingredients, as subsequently shown, were incorporated into the vulcanizates by swelling them to the required extent in a toluene solution of the ingredient followed by removal of the toluene by evaporation at room temperature. By proper adjustment of the concentration it was possible to incorporate the desired amount of additive. Upon removal of the toluene the *original* physical properties of the specimens were found to be affected only slightly by this treatment.

RELATION OF CURING SYSTEM AND ANTIOXIDANT TO AGING

The aging of inhibited and uninhibited peroxide and radiation cured vulcanizates is compared in Figure 1A. It is very evident that, in the absence of inhibitor, these vulcanizates have extremely poor age resistance. Since the radiation cured rubber *can* have *only* carbon to carbon crosslinks, and peroxide cured rubber is reported to have these also[11], it would appear that this type of crosslink is not intrinsically more resistant to aging as reflected by physical property changes in the vulcanizate.

As indicated earlier, the carbon-carbon crosslink is undoubtedly more stable chemically than other types of crosslinks, but this condition does not necessarily lead to improved age resistance since the stability of the crosslink may be relatively unimportant insofar as the age resistance of the vulcanizate is concerned. At least one other explanation may be advanced for the poor age resistance of these compounds, *viz.*, that a prooxidant is formed in the uninhibited vulcan-

izates during the curing process.   This possibility will be discussed in greater detail later in this paper.

The results of aging tests on inhibited and uninhibited SBR vulcanizates cured using accelerators only and a sulfur/accelerator combination are given in Figure 1B.   These data in combination with the data presented above clearly demonstrate that only the accelerator cured rubber has excellent age resistance, whether an inhibitor is present or not.   It is in the latter case that the question is most pertinent as to whether this greater age resistance, even without inhibitor, is conferred upon this vulcanizate because of the greater inherent stability of the network structure resulting from this curing system, or, whether some other factor is involved.

AGING OF VULCANIZATES CURED WITH ACCELERATORS ONLY

The data in Table III and the curves in Figure 2A illustrate aging results obtained using SBR cured with accelerator (DCPTTS plus MBT).   The very marked loss in aging resistance after acetone extraction of this "uninhibited" vulcanizate is most in evidence.   Impregnating the vulcanizate with an amount
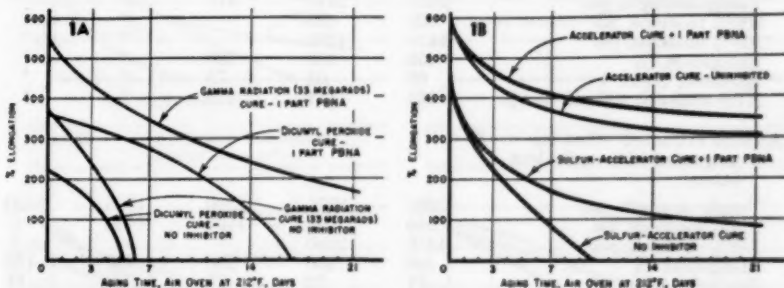
Fig. 1.—Air oven aging of inhibited vs. uninhibited peroxide and gamma radiation cured SBR compounds (A), and inhibited vs. uninhibited SBR sulfur and sulfur-type curing systems (B).

of extract equivalent to that removed by the acetone extraction (approximately 4% by weight) restores the excellent aging resistance.   The data in Table III show that the original properties of the acetone extracted vulcanizate do not differ drastically from those of the untreated vulcanizate.   These latter two conclusions demonstrate that the outstanding age resistance of this vulcanizate is due to the formation of an extremely active inhibitor formed from accelerator residues *in situ* during the curing process.

In the case of the TMTD cured natural rubber (discussed later) the bulk of the acetone extract was identified, by infrared analysis and melting point data, as zinc dimethyl dithiocarbamate (ZnDMDC).   This agrees with the findings of others[12-14].

The extract from SBR cured using DCPTTS plus MBT has not been positively identified as yet.   It does not appear to be any of the commercially available zinc dialkyl dithiocarbamates.   In view of the above findings, the acetone extracted vulcanizate was impregnated with one part of ZnDMDC prior to aging.   As shown in Table III and Figure 2A, the excellent age resistance of the original vulcanizate was almost completely restored.   When this vulcanizate was impregnated with a "conventional" antioxidant (PBNA), the

age resistance was improved somewhat over that of the acetone extracted sample, but not nearly to the extent of either the extract or the ZnDMDC impregnated vulcanizates. Results on the *inhibited* accelerator cured vulcanizate were nearly identical to those just described and therefore will not be reported upon in detail.

TABLE III

AGING OF SBR CURED WITH UNINHIBITED ACCELERATOR

		Days			
Time in air oven at 212° F	Original	3	7	14	21
Untreated vulcanizate					
Tensile strength, psi	2745	2790	2940	2380	2150
200% modulus, psi	380	645	925	980	700
300% modulus, psi	965	1645	2095	2210	1880
Elongation, %	590	430	400	320	310
Hardness, Shore A	70	69	68	70	69
NBS strain @ 400 psi, in %	171	137	131	125	115
Acetone extracted					
Tensile strength, psi	2535	2010	810	*	*
200% modulus, psi	520	450	—	*	*
300% modulus, psi	1410	1285	—	*	*
Elongation, %	450	380	120	*	*
Hardness, Shore A	68	68	78	*	*
NBS strain @ 400 psi, in %	185	154	118	*	*
Acetone extracted—then impregnated with equivalent extract					
Tensile strength, psi	2280	2375	2200	1965	1520
200% modulus, psi	650	1055	1190	1430	—
300% modulus, psi	1435	2260	—	—	—
Elongation, %	400	300	280	240	170
Hardness, Shore A	71	72	74	80	81
NBS strain @ 400 psi, in %	—	—	—	—	—
Acetone extracted—then impregnated with one part PBNA					
Tensile strength, psi	2465	2425	2505	1125	*
200% modulus, psi	550	775	755	—	*
300% modulus, psi	1435	1720	1755	—	*
Elongation, %	510	440	330	160	*
Hardness, Shore A	69	74	77	79	*
NBS strain @ 400 psi, in %	170	144	133	92	*
Acetone extracted—then impregnated with one part zinc dimethyl dithiocarbamate					
Tensile strength, psi	2425	2530	2415	2380	2160
200% modulus, psi	435	1190	1335	2140	—
300% modulus, psi	1315	2120	—	—	—
Elongation, %	480	340	290	230	200
Hardness, Shore A	67	68	70	74	78
NBS strain @ 400 psi, in %	183	113	99	76	62

* Samples too poor for testing.
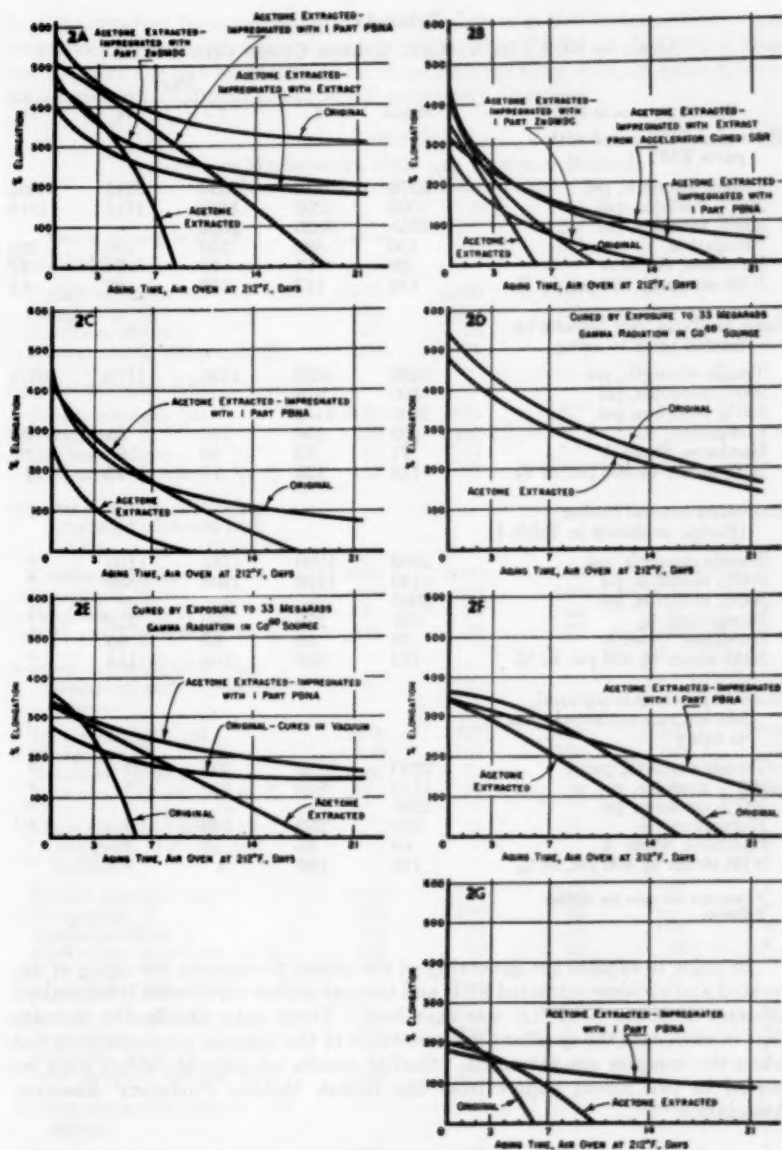
Fig. 2.—Air oven aging of uninhibited accelerator cured SBR compounds (A); uninhibited sulfur/accelerator cured SBR compounds (B); inhibited sulfur/accelerator cured SBR compounds (C); inhibited radiation cured SBR compounds (D); uninhibited radiation cured SBR compounds (E); inhibited peroxide cured SBR compounds (F); uninhibited peroxide cured SBR compounds (G).

TABLE IV

AGING OF SBR AND NATURAL RUBBER CURED WITH TMTD

Time in air oven at 212° F	Original	Days			
		3	7	14	21
Untreated SBR-cured with 3 parts TMTD					
Tensile strength, psi	3570	3770	3630	3315	3065
200% modulus, psi	1005	1200	1380	1715	1915
300% modulus, psi	2255	2820	3005	—	—
Elongation, %	430	380	350	280	260
Hardness, Shore A	69	71	73	74	77
NBS strain @ 400 psi, in %	140	117	106	89	85
Same as above, but acetone extracted prior to aging					
Tensile strength, psi	3290	3020	1180	1170	1010
200% modulus, psi	790	970	—	—	—
300% modulus, psi	2090	2470	—	—	—
Elongation, %	405	350	150	85	50
Hardness, Shore A	71	72	80	86	89
NBS strain @ 400 psi, in %	138	125	77	40	†
Untreated natural rubber (Recipe as shown in Table I)					
Tensile strength, psi	2390	1990	1785	1100	*
200% modulus, psi	1140	1310	1300	880	*
300% modulus, psi	2065	—	—	—	*
Elongation, %	330	270	250	210	*
Hardness, Shore A	70	69	67	65	*
NBS strain @ 400 psi, in %	122	105	104	114	*
Same as previous compound, but acetone extracted prior to aging					
Tensile strength, psi	2290	1270	390	*	*
200% modulus, psi	1110	840	420	*	*
300% modulus, psi	2200	—	—	*	*
Elongation, %	300	250	200	*	*
Hardness, Shore A	68	65	56	*	*
NBS strain @ 400 psi, in %	120	136	†	*	*

* Samples too poor for testing.
† Broke.

In order to explore the generality of the above phenomena the aging of untreated and acetone extracted SBR and natural rubber cured with tetramethylthiuram disulfide (TMTD) was examined. These data (Table IV) indicate that in each case the excellent age resistance of the original vulcanizates is lost when the samples are extracted. Similar results on natural rubber were reported in two recent papers from the British Rubber Producers' Research Association[15–16].

SULFUR/ACCELERATOR CURED VULCANIZATES

Results on the aging of uninhibited sulfur/accelerator cured SBR and natural rubber are presented in Table V and Figure 2B. In this case again, the acetone extracted vulcanizates show the poorest age resistance. It appears

that the residues from curing function as inhibitors in this instance also.   Impregnation of an extracted vulcanizate with either PBNA or ZnDMDC does not improve the age resistance as much as impregnating with an extract from SBR cured with DPCTTS plus MBT previously discussed.

TABLE V

AGING OF UNINHIBITED SBR AND NATURAL RUBBER
CURED WITH SULFUR/ACCELERATOR

Time in air oven at 212° F	Original	Days			
		3	7	14	21
Untreated SBR					
Tensile strength, psi	2625	2320	1640	1100	*
Elongation, %	450	220	80	—	*
Hardness, Shore A	67	76	—	—	*
NBS strain @ 400 psi, in %	158	74	—	—	*
Acetone extracted SBR					
Tensile strength, psi	2155	1675	*	*	*
Elongation, %	350	180	*	*	*
Hardness, Shore A	63	77	*	*	*
NBS strain @ 400 psi, in %	142	88	*	*	*
Acetone extracted SBR—impregnated with one part PBNA					
Tensile strength, psi	2720	2690	1705	945	*
Elongation, %	410	260	140	70	*
Hardness, Shore A	71	79	82	92	*
NBS strain @ 400 psi, in %	139	93	77	39	*
Acetone extracted SBR—impregnated with equivalent extract					
Tensile strength, psi	2545	1825	1965	1320	1080
Elongation, %	320	210	150	100	70
Hardness, Shore A	65	76	78	80	82
NBS strain @ 400 psi, in %	137	71	58	45	36
Acetone extracted SBR—impregnated with one part ZnDMDC					
Tensile strength, psi	2155	1735	1545	785	*
Elongation, %	280	130	80	—	*
Hardness, Shore A	65	78	79	84	*
NBS strain @ 400 psi, in %	135	52	48	30	*
Untreated natural rubber					
Tensile strength, psi	2260	910	*	*	*
Elongation, %	350	250	*	*	*
Hardness, Shore A	67	66	*	*	*
NBS strain @ 400 psi, in %	138	130	*	*	*
Acetone extracted natural rubber					
Tensile strength, psi	1880	100	*	*	*
Elongation, %	300	180	*	*	*
Hardness, Shore A	70	54	*	*	*
NBS strain @ 400 psi, in %	128	†	*	*	*

* Samples too poor for testing.
† Broke.

It will be observed that the aging of the extracted vulcanizates is, at least qualitatively, the same in the case of both the accelerator (Table III) and sulfur/accelerator cures (Table V). This fact suggests that the superior age resistance of the accelerator cured vulcanizate is dependent primarily on the presence of a very efficient inhibitor formed *in situ* during vulcanization, *or* that certain network structures are *per se* more susceptible to inhibition by specific types of

TABLE VI

AGING OF RADIATION–CURED SBR

Time in air oven at 212° F	Original	Days			
		3	7	14	21
Inhibited—untreated					
Tensile strength, psi	2450	2680	2640	1330	760
200% modulus, psi	370	585	800	625	—
300% modulus, psi	1650	1450	1840	—	—
Elongation, %	540	420	350	250	170
Hardness, Shore A	67	68	68	70	71
Inhibited—acetone extracted					
Tensile strength, psi	2540	2395	1910	1360	1065
200% modulus, psi	690	660	730	1065	—
300% modulus, psi	1595	1605	1665	—	—
Elongation, %	490	390	310	220	150
Hardness, Shore A	70	70	73	75	75
Uninhibited—untreated					
Tensile strength, psi	2980	2230	*	*	*
200% modulus, psi	885	760	*	*	*
Elongation, %	370	240	*	*	*
Hardness, Shore A	70	67	*	*	*
Uninhibited—acetone extracted					
Tensile strength, psi	2950	2740	1390	450	*
200% modulus, psi	1470	1220	1175	—	*
Elongation, %	340	290	210	80	*
Hardness, Shore A	74	74	75	78	*
Uninhibited—Acetone extracted —impregnated with one part PBNA					
Tensile strength, psi	3045	3110	2835	1750	1285
200% modulus, psi	1260	1340	1615	1625	—
Elongation, %	340	290	260	200	170
Hardness, Shore A	73	74	76	77	79
Uninhibited—cured in vacuum					
Tensile strength, psi	3070	2870	1560	1445	1010
220% modulus, psi	1590	1375	1410	—	—
Elongation, %	290	230	190	170	150
Hardness, Shore A	67	69	70	71	72

* Samples too poor for testing.

inhibitors. The fact that extracted accelerator cured rubber is improved in age resistance to a much greater degree than is extracted *sulfur/accelerator* cured rubber, when both are impregnated with ZnDMDC, is evidence toward the latter conclusion.

In Figure 2C some results on aging of inhibited sulfur/accelerator cured SBR are provided. Observations relating to these data are approximately the same as for the uninhibited compound just discussed.

SBR CURED WITH GAMMA RADIATION

Results of aging tests on radiation-cured SBR are furnished in Table VI and Figures 2D and 2E. In Figure 2D it is shown that the inhibited radiation-cured SBR, in contrast with rubbers based upon the types of cures discussed above, resists aging as well after acetone extraction as before. Since unin-

TABLE VII

AGING OF PEROXIDE CURED SBR

Time in air oven at 212° F	Original	Days			
		3	7	14	21
Inhibited—untreated					
Tensile strength, psi	2810	2815	2420	590	*
200% modulus, psi	760	945	1075	—	*
Elongation, %	360	330	290	120	*
Hardness, Shore A	71	72	74	74	*
Inhibited—acetone extracted					
Tensile strength, psi	2935	2470	1445	640	*
200% modulus, psi	825	1250	—	—	*
Elongation, %	350	280	200	60	*
Hardness, Shore A	71	73	76	84	*
Inhibited—acetone extracted— impregnated with one part PBNA					
Tensile strength, psi	2840	2845	2380	1540	1145
200% modulus, psi	975	1360	1410	—	—
Elongation, %	340	310	270	190	120
Hardness, Shore A	72	74	77	78	81
Ininhibited—untreated					
Tensile strength, psi	2485	1195	*	*	*
Elongation, %	220	160	*	*	*
Hardness, Shore A	75	76	*	*	*
Uninhibited—acetone extracted					
Tensile strength, psi	1860	1515	800	*	*
Elongation, %	200	170	90	*	*
Hardness, Shore A	74	76	81	*	*
Uninhibited—acetone extracted —impregnated with one part PBNA					
Tensile strength, psi	2305	2040	1755	1190	1025
Elongation, %	190	170	140	110	90
Hardness, Shore A	77	78	80	81	82

* Samples too poor for testing.

hibited radiation-cured SBR was shown earlier (Figure 1A) to have extremely poor resistance to aging, it appears that the acetone extraction removed an ingredient harmful to good age resistance as well as the antioxidant.

Inasmuch as this radiation curing was conducted in the presence of oxygen, it is surmised that the prooxidant may be peroxide resulting from radiation curing in the presence of oxygen. The contribution of "frozen in" free radicals, formed during the radiation process, to this poor age resistance was also considered. However, the fact (as shown in Figure 2E) that radiation curing in the absence of oxygen results in a vulcanizate with good age resistance, makes the peroxide formation a more reasonable explanation.

It is also shown in this figure that acetone extraction of an *uninhibited* radiation cured SBR improves age resistance and that impregnation with PBNA yields further improvement.　The fact that inhibited radiation-cured SBR ages well even after acetone extraction, suggests the possibility that the very poor age resistance of the uninhibited radiation cured rubber is due to the presence of peroxide residues resulting from curing in the presence of oxygen and that the inhibitor is very active in combating these peroxides during the curing process.　Comparing Figure 2D with Figure 2E, it is evident that the acetone-extracted, *inhibited* rubber resists aging to a much greater extent than the acetone-extracted, *uninhibited* rubber.

Since it may be assumed that the efficiency of the extraction in removing prooxidants is the same in each case, it appears that the greater amount of inhibitor retained by the radiation cured inhibited rubber (see Table II) may be effective in improving the age resistance of this compound.　It is possible that this "retained" inhibitor has become permanently fixed to the polymer chains by a grafting process during the radiation and is consequently no longer acetone extractable.

PEROXIDE–CURED SBR

The data on aging of various peroxide-cured samples are given in Table VII and Figures 2F and 2G.　As indicated in Figure 2F, acetone extraction of an *inhibited* vulcanizate in this case makes the age resistance slightly poorer.　In contrast with this observation, it is shown in Figure 2G that acetone extraction of an uninhibited sample improves age resistance slightly.　The best aging in each instance is obtained using the rubber which has been first extracted with acetone and then impregnated with antioxidant before the aging tests were run.

From these data it would appear that the peroxide-cured SBR contains a residual ingredient or ingredients which behave as prooxidants thereby interfering with age resistance of the vulcanizates.　In the case of the inhibited compound removal of these prooxidants by acetone extraction is invariably accompanied by removal of the antioxidant.　Since the net effect is slightly poorer age resistance, it is apparent that the beneficial action of the antioxidant outweighs the harmful effects of the prooxidant.　However, where no inhibitor is present (Figure 2G) acetone extraction (removal of prooxidant) invariably results in better age resistance.　As mentioned above, addition of antioxidant to an extracted vulcanizate yields the greatest improvement since the antioxidant is in this case available for protecting the vulcanizate and is partially consumed in counteracting the effects of the "residual peroxides" which were left in peroxide-cured SBR.

SUMMARY AND CONCLUSIONS

It has been shown that the age resistance of elastomeric vulcanizates is influenced to a very marked degree by residues formed *in situ* in the vulcanizate during the curing process.　By a dual process of removal of these residues and incorporation of selected ingredients subsequent to vulcanization, it has been shown that age resistance (as measured by accelerated oven-aging tests at 212° F) in rubbers cured by sulfur and/or sulfur bearing accelerators, is a prime function of these residues and nearly independent of the stability of the network structure.

An extremely active inhibitor is formed *in situ* during vulcanization of SBR and natural rubber using thiuram accelerators.　This inhibitor can be used to

"reinhibit" acetone-extracted accelerator-cured rubber. When added to sulfur/accelerator, peroxide, or radiation-cured vulcanizates, it improves their age resistance, but only in the case of the sulfur/accelerator cured rubber is this improvement better than with conventional inhibitors. This leads to the conclusion that the efficiency with which an inhibitor protects a vulcanizate varies widely, and conversely it appears that certain types of network structures are more readily protected or that certain inhibitors can function more efficiently in the protection of certain structures than others.

In the case of natural rubber cured with TMTD (zinc oxide present), the bulk of the accelerator residue is ZnDMDC, and this residue has been shown to function as a very efficient antioxidant when incorporated into acetone-extracted, accelerator-cured vulcanizate. It is no more effective than conventional inhibitors, however, when incorporated into an acetone-extracted, sulfur/accelerator-cured vulcanizate. Finally, it has been shown that acetone extraction of the various vulcanizates may lead to improvement or worsening of their age resistance, depending upon the nature of the residues resulting from the curing process.

ACKNOWLEDGMENT

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MEASUREMENT OF THE AGING OF
RUBBER VULCANIZATES *

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INTRODUCTION

The aging of rubber vulcanizates has received the attention of many workers and has been the subject of two symposia[1, 2] and a monograph[3]. It has been generally assessed from changes in tensile properties resulting from conditioning at elevated temperatures for specified periods of time. For historical reasons, greater attention has been given to changes in tensile strength than to changes in the other tensile properties. This emphasis probably resulted from the usefulness of this property in predicting the aging behavior of natural rubber vulcanizates.

A study of the results reported in the literature by Schoch and Juve[4], Buist[3], and others reveals that tensile strength is of little or no value in predicting the aging of synthetic rubber vulcanizates. Upon aging or conditioning at elevated temperatures the tensile strength of these vulcanizates may remain essentially unchanged or even increase. Similarly, the change in modulus or stiffness is not a consistent indicator of the aging process. Synthetic rubber vulcanizates generally become harder on aging; whereas natural rubber vulcanizates may become either harder or softer depending on the conditions and the particular vulcanizate. On the other hand, the ultimate elongation or strain at failure of both natural and synthetic rubber vulcanizates consistently decreases on aging. It is surprising that this property has not received more attention since it is unique for distinguishing elastomers from other materials and is the most valuable of the tensile properties for determining the utility of a rubber compound for a particular application. Further, this property appears to change upon aging in some semblance of an orderly manner. This paper presents a study of this change. The study is restricted to an aging test conducted on a nitrile-butadiene rubber (NBR) vulcanizate at NBS and to the results for the various rubber compounds reported by Schoch and Juve[4]. In all tests, the ultimate elongation is measured on dumbbell-shaped specimens having a cross section in the constricted part approximately 0.25 by 0.08 in. and bench marks 1-in. apart (Die C, ASTM Designation D412-51T[5]).

EXPERIMENTAL PROCEDURES

Vulcanizates of NBR were prepared in accordance with the procedure for formulation 1E in ASTM Designation D15-57T[5]. NBS standard materials for rubber compounding were used except for the rubber which was a sample of Hycar 1042. For each temperature of aging, three mixes were prepared and

TABLE I

TEMPERATURES AND PERIODS OF AGING

Aging temp., °C	Period of aging (in days)					
	A	B	C	D	E	F
23	0	100	377	(a)	(a)	(a)
34	0	30	120	270	(a)	(a)
45	0	10	41	90	160	359
57	0	4.9	12.9	51	79	113
70 (a)	0	1	4	9	16	25
70 (b)	0	5	20	46	81	148
85	0	1.21	2.71	4.83	12	15.7
100 (a)	0	0.110	0.375	0.90	1.64	2.67
100 (b)	0	.67	2.67	6	10	16.7

a Test still in progress.

blended. From the blended batch, 16 standard sheets (approximately 15 × 15 × 0.2 cm) were vulcanized for 40 min at 150° C. Six specimens were cut from each sheet using Die C, ASTM Designation D412-51T[5]. One specimen from each sheet was tested the day after vulcanization. Another specimen from each sheet was tested after each of five prescribed periods of aging at a particular temperature. The position of the specimen in the sheet was noted. The specimens selected for any one period of aging were approximately equally divided among outside, center, and intermediate positions in the 16 sheets. Five periods of aging at each of seven temperatures were used in this study, as shown in Table I.

RESULTS

The mean value for each set of 16 specimens comprising the test under each prescribed condition of time and temperature is given in Table II. In order to have a basis for studying these results, it is necessary to know the magnitude of the error. Table III gives the analysis of variance for the nine groups of unaged specimens. It is inferred from this analysis that the standard deviation of a specimen taken at random from one of the 16 sheets comprising a batch is 30 per cent elongation or a coefficient of variation of 4.8 per cent. Perhaps a more pertinent measure of error is the one derived from the mean square for the

TABLE II

ULTIMATE ELONGATIONS OF NBR VULCANIZATE AFTER PRESCRIBED CONDITIONS OF AGING

Aging temp., °C	Elongation after period of aging[a]					
	A %	B %	C %	D %	E %	F %
23	652	604	528	—	—	—
34	623	580	534	475	—	—
45	609	576	532	494	465	394
57	614	563	513	436	402	404
70 (a)	596	593	548	527	480	433
70 (b)	626	496	420	359	305	251
85	609	532	461	419	342	321
100 (a)	656	581	548	461	418	371
100 (b)	654	489	353	249	152	67

a See Table I for duration of period.

TABLE III

ANALYSIS OF VARIANCE—UNAGED SPECIMENS

Source of variation	Degrees of freedom	Mean square	Component of variance
Between batches	8	7947	439
Within batches	135	921	921

interaction between sheets and aging times. Table IV gives this information for each of the nine batches. The average coefficient of variation of 5.7 per cent is somewhat larger than the 4.8 per cent noted above since it includes variability introduced by aging. However, it is not larger than the 5.9 per cent coefficient of variation for a specimen taken at random from any batch. Thus, the design of test makes the experiment more efficient than a complete random selection of specimens for all batches. Since 16 specimens are used for each aging condition, the overall coefficient of variation is about 1.4 per cent.

It is seen in Table I that two batches were tested at both 70° and 100° C. The purpose of the second batch is to obtain data under conditions of more extensive aging. In the case of the second batch tested at 100° C, the ultimate elongation is reduced much more than that for any of the other batches, being less than 100 per cent after the longest period of aging.

Attempts to express the data in Table II by the standard kinetic equations for a first or a second order reaction were not successful. Other mathematical expressions of the form

$$y = Ae^{-Bt^n} \text{ and } y = Ae^{-Bt} + Ce^{-Dt}$$

were tried. The latter expression described the data well for long periods of aging, but it did not satisfactorily account for the early part of the curve. Further, this equation was difficult to apply. Therefore, the data were empirically fitted to a power series of the form:

$$y = a + bx + cx^2 + dx^3 + \dots \tag{1}$$

It was observed that when $x = \sqrt{t}$ and y is the ultimate elongation, the first two terms in this series satisfactorily expressed the data in Table II except for the last three points of the second batch at 100° C were less than half of the

TABLE IV

ESTIMATION OF VARIABILITY DERIVED FROM INTERACTION OF SHEET AND AGING TIME

Aging temp., °C	Mean elong. %	Mean square	Coefficient of variation %
23	595	1132	5.6
34	553	762	5.0
45	512	667	5.0
57	489	821	5.9
70 (a)	530	824	5.4
70 (b)	409	899	7.3
85	447	734	6.1
100 (a)	506	604	4.9
100 (b)	327	494	6.8
		771 avg.	5.8 avg.
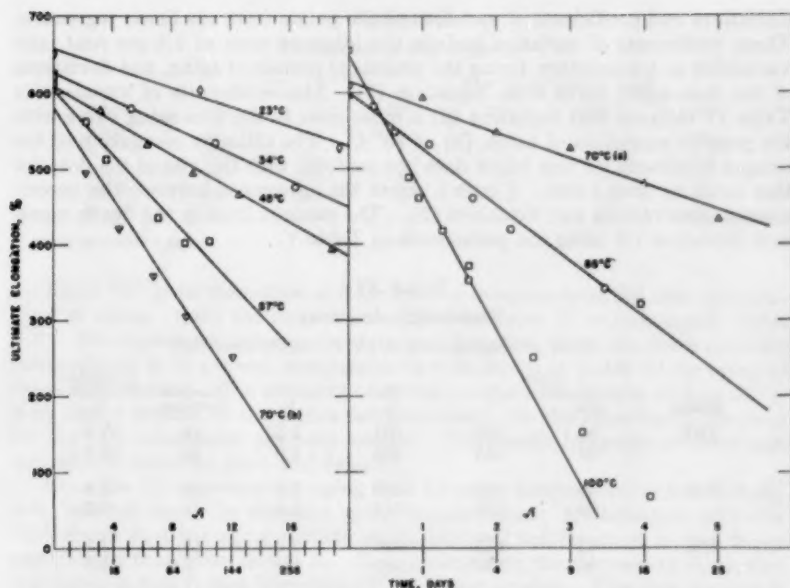
FIG. 1.—Effect of aging at various temperatures on ultimate elongation of rubber vulcanizates. The straight lines represent the least square linear regression for each temperature. The last three points at 100° C are not included in the regression.

original elongation remained. Accordingly, a study was made of the general applicability of the following simplified equation for expressing the change in elongation upon aging:

$$E = E_0 - k\sqrt{t} \tag{2}$$

where E = ultimate elongation after aging for time t, and E_0 and k are parameters of the vulcanizate.

Table V gives the values of the parameters E_0 and k calculated by the method of least squares from the data in Table II. This table also gives the standard

TABLE V
REGRESSION ANALYSIS
NBS data on NBR vulcanizates

Aging temp., ° C	E_0 %	k	Standard deviation	Coefficient of variation %
23	657	6.4	13.5	2.3
34	626	8.9	5.9	1.1
45	608	11.4	3.8	0.7
57	603	21.1	19.0	3.9
70 (a)	613	33.6	14.5	2.7
70 (b)	581	29.8	34.0	8.3
85	600	74.2	16.5	3.7
100 (a), (b)[a]	647	180.4	11.7	2.3

[a] Omitting three longest periods of aging.

deviations and coefficients of variation of the points from the linear regression. These coefficients of variation include the inherent error of 1.4 per cent, any variability in temperature during the prolonged periods of aging, and deviations of the true aging curve from Equation (2). The coefficients of variation in Table IV indicate that Equation (2) is quite close to the true aging curve with the possible exception of batch (b) at 70° C. The ultimate elongation of the unaged specimens for this batch does not conform with the rest of the data for this batch at later times. Figure 1 shows the agreement between the experimental observations and Equation (2). The straight lines in the figure represent Equation (2) using the parameters in Table V.

TABLE VI
REGRESSION ANALYSIS
Test A[a]—aging data at 25° C (approximately)

Rubber	Cure		E_0 %	k	Standard deviation	Coefficient of variation %
	Min	° C				
SBR	60	135	601	4.5	16	3.4
	90	135	553	4.9	44	10.9
NR	45	135	669	5.0	16	3.1
	90	135	614	5.9	13	3.0
CR	45	143	528	2.8	15	3.4
	90	143	499	2.9	7	1.8
NBR	45	135	517	2.5	22	4.9
	90	135	485	2.2	6	1.5
IIR	20	149	530	0.4	19	3.6
	30	149	465	1.4	15	3.6

[a] See references 4 and 6.

INTERLABORATORY TEST

The results of the interlaboratory test reported by Schoch and Juve[4, 6] were studied. In test A of this report, there were five compounds made from different rubbers. In test B, there were also five compounds, three of which were made from natural rubber (NR), one from NBR, and one from styrene-butadiene rubber (SBR). Since the paper by Juve and Schoch[6] was published, data for test A have become available through Subcommittee 15 of ASTM Committee D-11, on aging at room temperature for 8 years. Data for the 35- and 180-min cures of the SBR compound have also become available.

Table VI summarizes the results obtained by applying Equation (2) to the ultimate elongation data of test A for aging at room temperature up to 8 years. Except for the 90-min cure of the SBR compound Equation (2) represents the data quite well. The data for the SBR 90-min cure are very erratic and not consistent with other aging data for this vulcanizate.

Examination of the values of k in Table VI for different cures of the same compound indicates that the change in elongation during aging is not dependent on the cure except for butyl rubber (IIR). The k values for the 35- and 180-min cures of the SBR compound are about the same as those in Table VI for the 60- and 90-min cures. This independence of k is also observed for all four cures at aging temperatures of 70° and 100° C. At 121° C, k decreases with time of cure possibly as a result of concomitant vulcanization.

TABLE VII
VALUES OF k FOR TEST A[a]

Rubber	Cure		k for temperature of aging			
	Min	°C	25° C	70° C	100° C	121° C
SBR	90	135	4.9	36	117	295
NR	90	135	5.9	54	179	363
CR	90	143	2.9	20	69	162
NBR	90	135	2.2	34	85	172
IIR	30	149	1.4	32	97	186

[a] See references 4 and 6.

Table VII gives the values of k for the five compounds at the four temperatures of aging. Only the longest cure listed in Table VI is included in Table VII. The agreement between the data and Equation (2) at the three elevated temperatures is, in general, comparable to that shown in Table VI for aging at room temperature. The anomaly observed for the SBR 90-min cure at 25° C is no longer present at the higher temperatures. On the other hand, the data for the IIR vulcanizate are very erratic. The erratic behavior of these vulcanizates is noted by Juve and Schoch[6].

Equation (2) expresses the aging data for room temperature of test B fairly well, but not those for elevated aging temperatures. Examination of Table VIII shows that the aging periods at the elevated temperatures in test B are much longer than those in test A. As a consequence, the decrease in elongation is so large in test B that Equation (2) no longer applies. The data for test B are too limited and erratic to apply the more general Equation (1).

EFFECT OF TEMPERATURE

If the decrease in ultimate elongation upon aging is the result of a single chemical reaction, the parameter k in Equation (2) may be treated as a reaction rate constant. According to the Arrhenius equation

$$\ln k = \frac{-\Delta H}{RT} + c$$

a plot of the logarithm of k versus the reciprocal of the absolute temperature of aging should be linear. Figure 2 is such a plot of the data in Tables V and VII,

TABLE VIII
AGING CONDITIONS IN INTERLABORATORY TESTS[a]

Test	Room temp., yr	70° C hr	100° C hr	121° C hr	125° C hr	150° C hr
A	1	96	24	6	—	—
	2	168	48	18	—	—
	3	336	96	24	—	—
	4	672	168	48	—	—
	8	—	—	—	—	—
B	1	512	64	—	12	2
	2	1024	128	—	24	4
	4	2048	256	—	48	8
	—	4096	512	—	96	16

[a] See references 4 and 6.

excluding the IIR compound which behaved erratically at temperatures of 70° C and higher. The curves for the compounds of test A appear to be linear. On the other hand, the curve for the NBR compound studied at NBS definitely is not linear. As the temperature increases, the rate of aging increases much faster than predicted by the Arrhenius equation. When there is curvature, prediction of shelf aging from aging tests at elevated temperature is extremely hazardous.
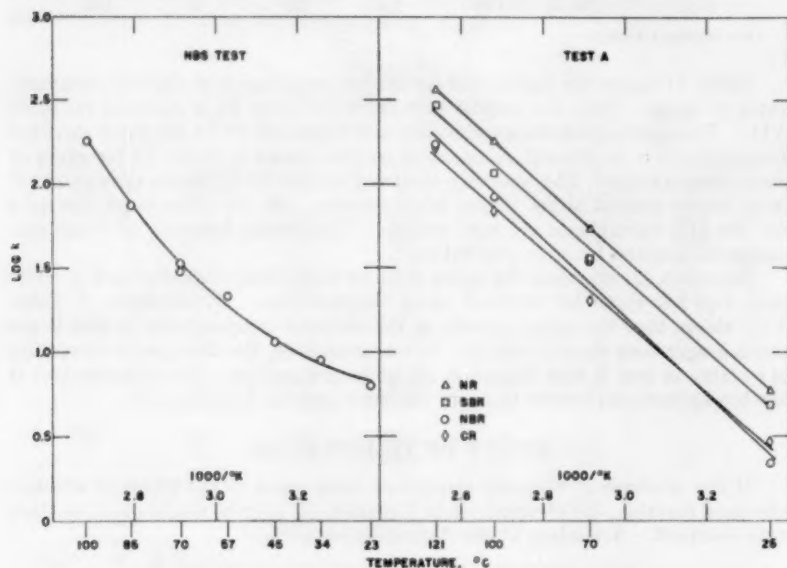
Fig. 2.—Effect of temperature on aging of rubber vulcanizates. The straight lines for test A represent the least square linear regressions.

The slopes in Figure 2 are related to the energies of activation. The values calculated for the rubber compounds of test A are: NR 20,500 cal/mole, SBR 19,600 cal/mole, CR 19,400 cal/mole, and NBR 22,100 cal/mole. These values are in reasonable agreement with those reported by Juve and Schoch[6] for the 90-min cures, calculated from equal changes in ultimate elongation.

CONCLUSIONS

Ultimate elongation (strain at failure) can be used to assess the aging of all rubber vulcanizates. For this purpose, it appears that Equation (2) can be used to express the early part of the aging process, corresponding to a period of aging at room temperature of 10 or more years. Prediction of shelf aging from tests at two or more elevated temperatures is only possible if the relationship between aging and temperature is known. For some rubber compounds the Arrhenius equation appears to hold. In these instances, it provides an effective means for estimating shelf aging.

SYNOPSIS

A study of aging data in the literature and of measurements made at the National Bureau of Standards indicates that ultimate elongation is the best of the tensile properties for characterizing the deterioration of rubber vulcanizates during storage at various temperatures. Ultimate elongation (strain at failure) decreases during aging for all types of rubber vulcanizates, whereas tensile strength and modulus may increase, decrease, or remain essentially unchanged.

This study includes measurements of ultimate elongation of a nitrile rubber vulcanizate after various periods of storage at temperatures of 23°, 34°, 45°, 57°, 70°, 85°, and 100° C. It also includes a study of the published data on ultimate elongation obtained in an interlaboratory test conducted by Subcommittee 15 of ASTM Committee D-11, involving vulcanizates of five different rubbers stored at 25°, 70°, 100°, and 121° C.

The change in ultimate elongation over prolonged periods of storage cannot be expressed by a simple mathematical equation. However, during most of the useful storage life of a rubber vulcanizate, the elongation decreases approximately linearly with the square root of time. The data indicate that for some vulcanizates an estimate of storage life at room temperature can be made from measurements of ultimate elongation at two or more elevated temperatures.

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IMPORTANT STABILITY FACTORS FOR
STYRENE-BUTADIENE RUBBER *

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INTRODUCTION

Unlike raw natural rubber which contains naturally occurring antioxidants, styrene-butadiene rubber (SBR) is quite susceptible to oxidative degradation unless special precautions are taken to stabilize the polymers[1, 2, 3]. This fact is recognized by manufacturers of the synthetic polymer and standard practice throughout the industry includes the incorporation of 1.25 parts of a stabilizing agent in the polymer during manufacture. Initially, diarylamine compounds such as phenyl-2-naphthylamine and certain diphenylamine reaction products were used for the purpose. The staining and pigmenting nature of these chemicals permitted the manufacture of only relatively dark colored products from the polymers containing these materials. Appreciation of the possibilities of white or light colored polymer led to the development of a number of non-staining SBR stabilizers. Two of these have been widely used in production of nonstaining grades of SBR. These are tris(nonylated phenyl) phosphite (Polygard)[4] and styrenated phenol (Wingstay-S, Agerite Spar and Styphen I). Tris(nonylated phenyl) phosphite is particularly effective in retarding changes which occur when SBR polymer is subjected to heat and this product is currently being widely used in the United States and elsewhere as a preferred non-discoloring SBR stabilizer. The effects of various SBR stabilizer types have been compared in several studies[2, 5, 6, 7].

Although the presence of an effective stabilizing agent is a prime factor in preventing heat degradation of SBR polymer, it can be shown that other factors also influence the stability of the polymer. It has been demonstrated that the conditions of flocculation, for example, may have a definite effect on the heat resistance of the polymer[8, 9, 10]. In the present work the stability of SBR has been related to the amount of sodium chloride used in the conventional salt-acid coagulation method. The presence of certain metallic ions appears to have a pronounced effect on polymer stability.

DEFINITIONS

In considering the matter of SBR stabilization, a clarification of terminology appears to be desirable. As applied in the present discussion the term "stabilizer" is used in reference to the protection of the polymer during manufacture in the polymer plant, during shipping and storage and during those processing operations in the fabricators plant prior to vulcanization. Protection of the

vulcanizate, in the present terms of reference, is accomplished by the use of "antioxidants." Stabilizers, according to this terminology, are specifically designed to protect the raw polymer while antioxidants are used to protect the cured vulcanizate. Under these definitions the measurement of the effectiveness of SBR stabilizers will be indicated in tests in which the raw polymer is subjected to heat or other aging influences whereas the effectiveness of antioxidants will be indicated in tests involving the aging of vulcanizates.
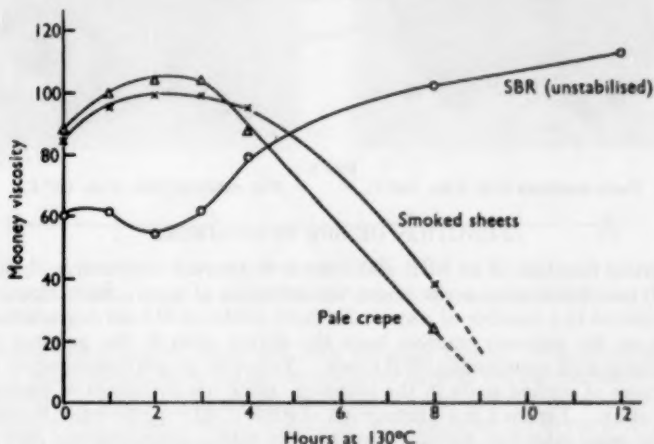
Fig. 1.—Effect of heat on Mooney viscosity of natural rubber and unstabilized SBR.

The suggested distinction between stabilizers and antioxidants is useful in approaching the selection of chemicals as protective agents for SBR. It has been our own experience that conventional nonstaining antioxidants for natural rubber vulcanizates are not necessarily the most effective nonstaining stabilizers for uncured SBR.

EFFECTS OF HEAT ON NATURAL RUBBER AND ON SBR

A simple comparison of the influence of heat on raw natural rubber and on SBR brings out some significant differences between the polymers[2]. In Figure 1 are plotted the Mooney viscosities of pale crepe, smoked sheet and unstabilized SBR 1503 polymer after several periods of aging in the 130° C oven. With both natural rubber samples there is observed an initial increase in viscosity which is followed by a rather sharp drop in Mooney viscosity. In the case of unstabilized SBR is seen some peculiar aberrations in the viscosity during early stages of heating which is followed by progressive hardening of the polymer. It is evident that the predominating effect of heat on natural rubber polymer is one of softening whereas with SBR the predominating effect is one of hardening[3]. Stated in another way, the effect of heat on natural rubber is predominately one in which the polymer chain is broken into lower molecular weight fragments. With SBR the predominating result is one of crosslinking and formation of higher molecular weight species exhibiting limited solubility in benzene (gel).
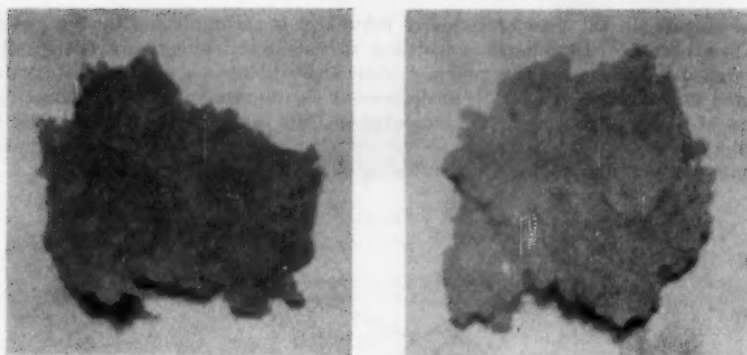
Poorly stabilized SBR; 2 hrs. 110° C.   Well stabilized SBR; 2 hrs. 110° C.

FUNCTION OF SBR STABILIZERS

A prime function of an SBR stabilizer is to prevent destructive changes in the polymer which may occur under the influence of heat. Such changes become evident in a number of ways. An early evidence of heat degradation can be seen as the polymer emerges from the drying oven in the polymer plant, particularly with nonstaining SBR types. Yellow to brown discoloration or the appearance of melted spots in the polymer crumb are evidences of inadequate stabilization. Figure 2 is a photograph of SBR 1502 type polymer flocculated from the same latex but stabilized in one case with a comparatively ineffective stabilizer (left) and in the other case with tris(nonylated aryl) phosphite (right). The photograph shows the difference in appearance after drying samples of the polymer crumb for 2 hours in a 110° C circulating air oven. Another example is given in Figure 3 which illustrates the influence of drying

Fig. 3.—Effect of drying temperature on SBR 1502.
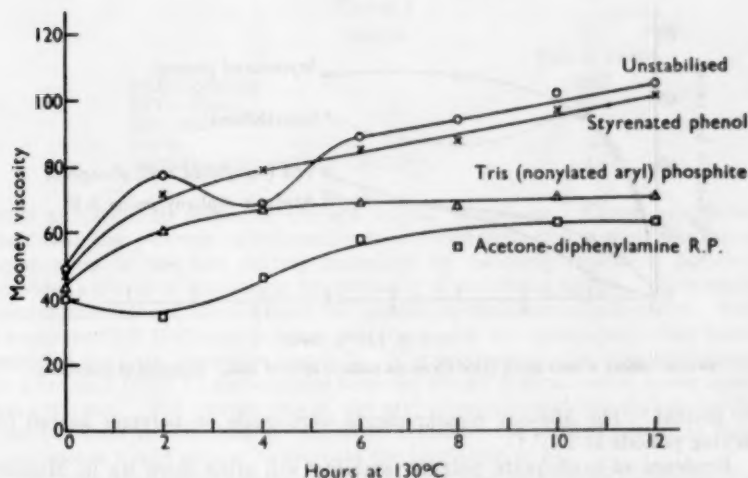
Fig. 4.—Effect of heat on Mooney viscosity of SBR 1503. Influence of stabilizers.

temperature on polymers stabilized with different agents. The advantages of effective stabilization show up under the more drastic drying conditions.

Evidence of polymer instability may show up as definite heat softening of the polymer with consequent difficulties in removal from the dryer belts and in subsequent handling operations. Variability in Mooney viscosity will often be traced to inadequate stabilization. The several commercial SBR stabilizers will have differing effects on heat aging of the polymer as indicated in Mooney viscosity measurements. Typical viscosity curves are shown in Figure 4 in which data obtained on SBR 1503 stabilized with three commercial stabilizers
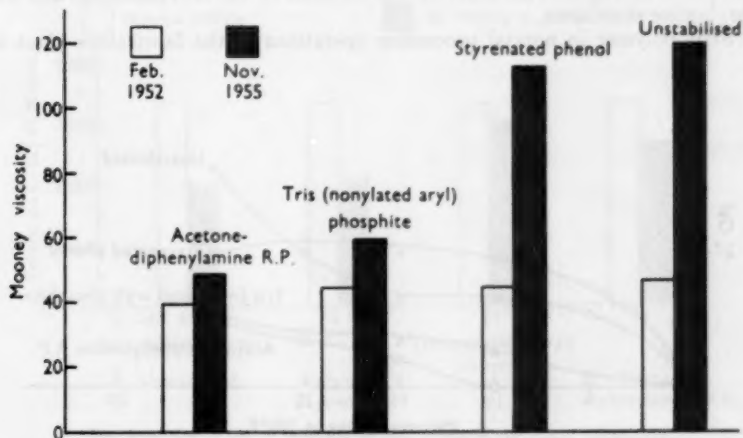
Fig. 5.—Effect of shelf aging on Mooney viscosity of SBR 1503. Influence of stabilizers.
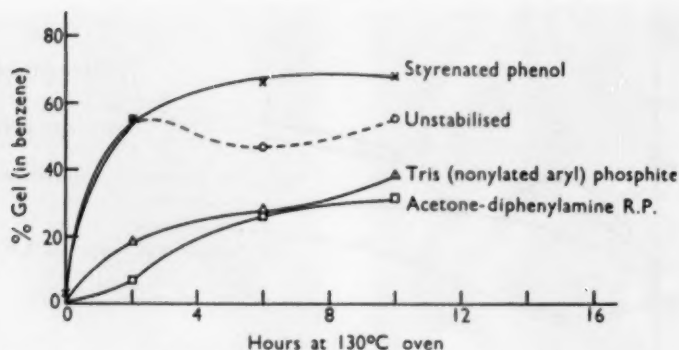
Fig. 6.—Effect of heat aging (130° C) on gel buildup of SBR 1503. Influence of stabilizers.

are plotted. The Mooney measurements were made on polymer heated for varying periods at 130° C.

Evidence of inadequate polymer stability will often show up in Mooney viscosity measurements after storage. The data obtained in one study are shown in Figure 5 in which Mooney viscosity values on freshly made polymer (February, 1952) and stabilized with three commercial stabilizers is compared with the Mooney values on the same polymers after greater than 3 years shelf aging (until November, 1955). The protective effect of the nondiscoloring phosphite stabilizer compares favorably with the conventional staining type stabilizer in this study.

As stated earlier, an important effect of heat on SBR is that of crosslinking in which benzene insoluble gel fractions are produced. The measurement of gel after 130° C heat treatment provides a means of comparing the effectiveness of stabilizing agents. In Figure 6 are plotted the gel values on SBR 1503 stabilized with the same stabilizing agents used in the previous comparison. Best protection against gel build-up was afforded by the aryl phosphite and the diarylamine stabilizers.

SBR polymer in normal processing operations in the fabricators plant is
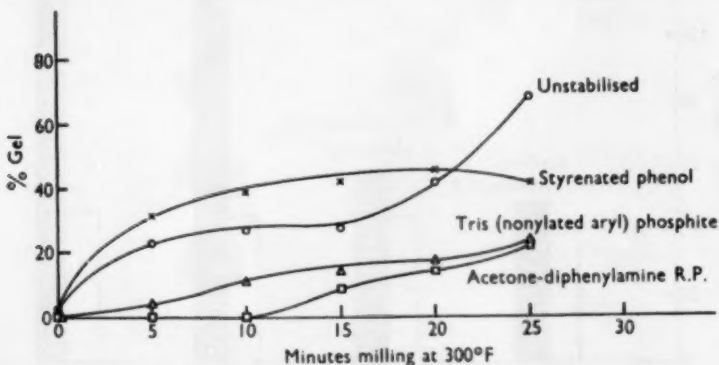
Fig. 7.—Effect of hot milling on gel buildup of SBR 1503. Influence of stabilizers.

TABLE I
RECIPE

	Parts by weight
SBR—polymer	100.0
EPC—Black	40.0
Zinc oxide	5.0
Sulfur	2.0
Benzothiazolyl disulfide (MBTS)	1.75

often subjected to rather severe hot milling operations. Unless adequately stabilized the polymer is vulnerable to deterioration under such treatment. Application of the hot milling technique to variously stabilized polymers provides a means of comparing the efficiency of stabilizing agents. Here again, measurement of gel offers a basis for comparing stabilizer effectiveness. Such a study on SBR 1503 type polymer stabilized with the agents previously tested provided the data plotted in Figure 7. The polymers in this case were placed on a hot mill (300° F) and samples removed for gel determination at the specified intervals. The advantages of the aryl phosphite and the diphenylamine type stabilizer in retarding gel are quite evident. Styrenated phenol in these experiments would appear to promote the formation of gel.

The development of a certain amount of gel may sometimes be beneficial in aiding the processing of the polymer. Likewise, oxidative breakdown of poorly stabilized polymer may appear to be advantageous in decreasing the power demands on mill breakdown. However, these advantages in processing characteristics are often attained at the expense of ultimate vulcanizate quality. An example of the adverse effects of gel buildup on vulcanizate properties is to be seen in the physical properties of vulcanizates prepared from hot milled polymers. SBR 1503 polymers stabilized with various stabilizing agents and flocculated by the salt-acid coagulation technique were prepared. Portions of each polymer were subjected to hot milling for 30 minutes on a 300° F mill. These polymers as well as portions of the original polymers which were not subjected to the hot milling treatment were compounded, using the recipe
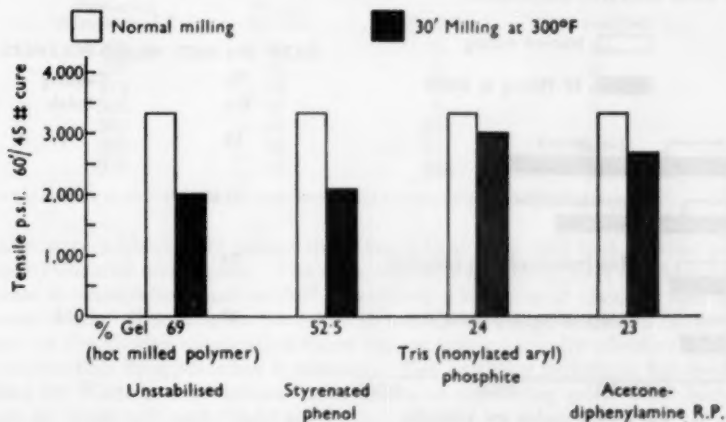
FIG. 8.—Effect of 300° F milling of polymer on tensile strength of vulcanizate. Influence of stabilisers.
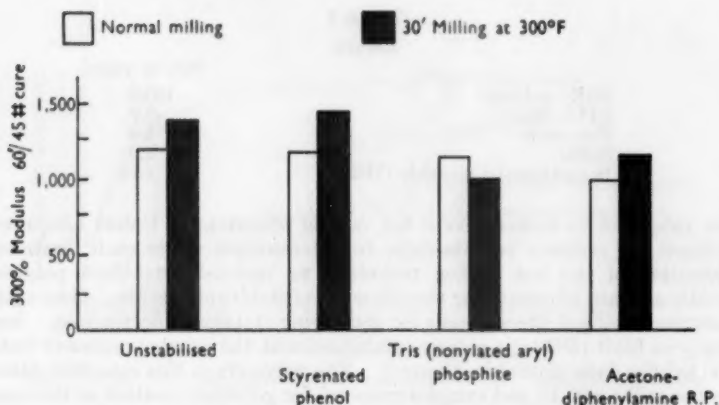
Fig. 9.—Effect of 300° F milling of polymer on modulus of vulcanizate.
Influence of stabilizers.

shown in Table I and cured for 30, 60, and 90 minutes at 292° F. The tensile properties were considered optimum on the 60 minute vulcanizate and the data plotted in Figures 8, 9, and 10 are based on this cure.

The tensile properties of the vulcanizates from both normally mixed and hot milled polymers are shown in Figure 8. Little difference is seen in the tensile strengths of the variously stabilized polymers prior to hot milling. The unusual protective action of the phosphite stabilizer during hot milling is shown in the tensile strength of the vulcanizate from the hot-milled polymer. The milled polymers giving the higher tensile values are those which show the least gel.

A comparison of the 300 per cent modulus values on the same vulcanizates is given in Figure 9. The prevention of modulus increase is characteristic of the more effective stabilizers.
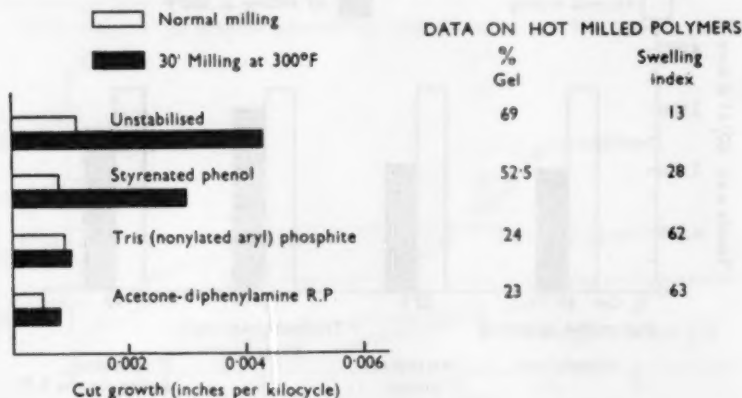
Fig. 10.—Effect of hot milling of polymer on cut growth of vulcanizate.
Influence of stabilizers.

A particularly valuable advantage of effective stabilization is seen in cut growth data on vulcanizates from hot milled polymer. It will be observed in Figure 10 that the cut growth values on normally milled polymers do not show appreciable differences between the stabilizers. The advantages of adequate stabilization become very evident, however, in cut growth measurements on the hot milled polymers. Poor cut growth is associated with higher gel content and also with low swelling index (tight gel). A discussion of gel as a definitive property in SBR technology has been presented by White[11].

TABLE II

EFFECT OF 350° F BANBURY MASTICATION ON GEL FORMATION

Time (min.)	Mooney viscosity[1]	% Gel	% Gel (remilled) (3 passes through cold mill)
3	55	0	0
6	52	12	0
9	47	25	20
12	46	34	30

ML-4 minutes at 212° F.

The important relationship between gel and physical properties of vulcanizates has been shown in an independent study in the laboratories of the J. M. Huber Corporation in the United States[12]. The work involved an investigation of the effects of hot Banbury mastication on gel formation in SBR polymer and included a study of the effects of gel on the physical properties of cured vulcanizates. In that study SBR 1500 polymer (stabilized with an acetone-diphenylamine reaction product (BLE)) was masticated at 350° F, and samples were removed at 3-minute intervals for Mooney and gel determinations. The

TABLE III

EFFECT OF MASTICATION TEMPERATURE ON GEL FORMATION

(12 minutes Banbury mixing at temperature indicated)

Mastication temperature, ° F	Mooney viscosity[1]	% Gel	% Gel (remilled)
225	43	0	0
250	44	0	0
275	43	0	0
300	45	0	0
325	48	23	0
350	54	34	30
375	42	41	40

[1] ML-4 minutes at 212° F. The Mooney viscosity of the unmasticated SBR 1500 was 45.

samples were subsequently passed three times through a cold mill and the gel content measured once again. The data obtained are reproduced in Table II. Increase in mastication time at 350° F produced a lowering of viscosity and an increase in gel. Remilling on the cold mill served to redisperse the gel initially formed at the shorter mastication times but was only partially effective when the mastication time exceeded 6 minutes. The remilling technique has been utilized by White and coworkers[11] as a means of classifying gel in SBR technology as "loose gel" and "tight gel."

The Huber study was extended to measuring the effects of mastication temperature on gel formation. The data obtained are given in Table III.

TABLE IV

EFFECT OF GEL ON PROPERTIES OF A TREAD STOCK

Mastication temperature, °F	% Gel	Modulus (200%)	Tensile	Elongation	Mooney viscosity	Demattia* flexing
225	0	1030	4320	510	67	39,000
250	0	1040	4230	500	67	35,000
275	0	1060	4120	480	63	34,000
300	0	1130	4040	457	60	25,000
325	25	1410	3980	405	72	7,000
350	42	1700	3640	380	84	4,500
375	50	1740	3300	305	?	3,500

* Flexes to produce 0.5 inch cut growth.

No gel was detected when the polymer was masticated in the Banbury for 12 minutes at temperatures up to 300° F. At 350° and 370° substantial amounts of tight gel were produced which was not redispersed by passing through a cold mill.

In the same investigation the Huber study included the effects of gel on cured properties of a tread stock. Vulcanizates prepared from polymers masticated in the Banbury at temperatures ranging from 225° to 375° F gave the physical properties shown in Table IV. It is to be observed that the 200 per cent modulus of the vulcanizates increases with increasing mastication temperature. Although no gel was detected in the polymer milled at temperatures under 325° F, the subtle effects of increasingly severe heat treatment are clearly evident in increasing modulus and in a decrease in tensile, elongation, and crack growth resistance. The adverse effects of gel are especially evident in the greatly reduced crack growth resistance of vulcanizates from polymers masticated at temperatures in excess of 300° F. The observed undesirable effects of processing heat on the physical properties of SBR vulcanizates serve to emphasize the importance of adequate polymer stability.

INFLUENCE OF STABILIZERS ON GEL BUILDUP IN OIL EXTENDED SBR POLYMER

Hot milling of commercially available oil extended SBR polymers stabilized with various stabilizers brings out some rather striking variations in gel buildup

TABLE V

EFFECT OF HOT MILLING ON GEL BUILDUP IN COMMERCIAL OIL EXTENDED SBR

Influence of stabilizers

Polymer	1703	1707	1708	1773	1778
stabilizer[1]	SP	Polygard	Polygard	HAP	SP
Oil, pts./100	25 Naphth.[1]	37½ Naphth.	37½ Naphth.	25 Naphth.	37½ Naphth.
Coagulation	Salt-acid	Salt-acid	Salt-acid	Salt-acid	Salt-acid
Emulsifier	Mixed-acid	Rosin-acid	Fatty-acid	Mixed-acid	Mixed-acid
		Per cent gel			
Time on 350° F mill					
0 min.	Nil	Nil	0.7	0.4	Nil
5 min.	21.9	Nil	Nil	23.2	26.0
10 min.	37.3	Nil	Nil	33.9	34.1
15 min.	39.9	Nil	1.8	40.5	41.4
20 min.	41.4	0.39	Nil	44.1	41.1

[1] SP = Styrenated phenol. Polygard = Tris(nonylated aryl) phosphite. HAP = Higher alkylated phenol. Naphth. = naphthenic oil.

characteristics. Polymers procured from various sources and containing three nonstaining type stabilizers were milled at 350° F for intervals from 5 to 20 minutes. Gel measurements were made on the samples after each milling treatment. The data are shown in Table V. Although the polymers differed some in the nature of the extending oil and in the emulsifier used in their preparation, the main difference as far as polymer stability is concerned can be attributed to the difference in the stabilizer. The effect of the phosphite type stabilizer in preventing gel buildup in hot milled oil extended polymer is exceptional.
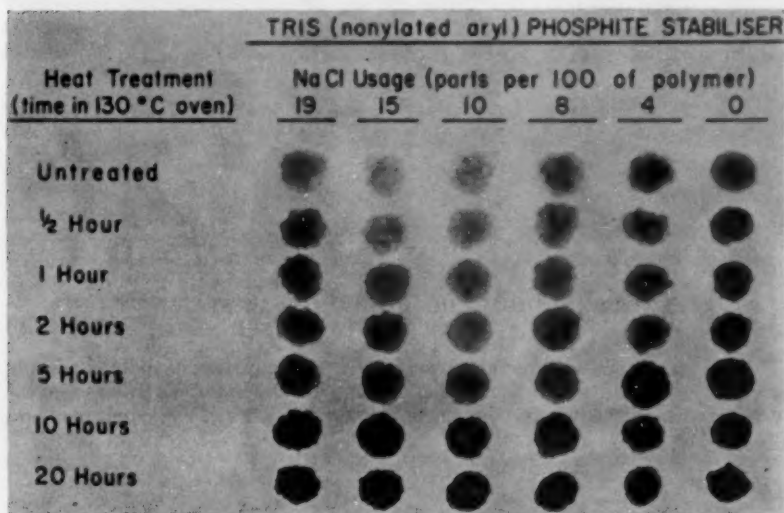
Fig. 11.—Effects of sodium chloride usage on heat stability of SBR 1503 (salt-acid flocculation).

EFFECTS OF FLOCCULATING CONDITIONS ON POLYMER STABILITY

Several investigations have shown that conditions used in flocculating SBR latex can exert a pronounced effect on the heat stability of the resulting polymer. Glasgow and Vila[8] demonstrated that SBR flocculated with salt and sulfuric acid exhibits poorer heat stability than polymer flocculated with sulfuric acid alone. The straight acid coagulation method is made commercially practical by the use of a small quantity of glue in the acid solution[13, 14]. Alum coagulated polymers also show improved heat stability when compared to polymer coagulated by the conventional salt-acid method[8, 10, 15]. Albert and coworkers have shown that the stability of alum coagulated polymers can be related to the amount of iron impurity present in the alum flocculant[15]. Other workers have also observed the promoting effects of iron upon the breakdown of SBR polymer[3, 15, 17, 18, 19]. Degradation in the presence of iron is particularly pronounced when the polymer is extended with oil[20, 21]. An enlightening discussion of the role of iron in the degradation of oil extended cold SBR is given by Reynolds[21].

Fig. 12.—Effects of sodium chloride usage on heat stability of SBR 1503 (salt-acid flocculation).

EFFECTS OF SODIUM CHLORIDE ON HEAT STABILITY OF SALT–ACID COAGULATED SBR

In the present study the influence of varying proportions of sodium chloride on the heat stability of conventionally salt-acid flocculated SBR has been investigated. In this work a commercial, cold SBR latex (1503 type), made on

Fig. 13.—Effects of sodium chloride usage on heat stability of SBR 1503 (salt-acid flocculation).

a sulfoxylate-diisopropylbenzene hydroperoxide system and short-stopped with sodium dimethyl dithiocarbamate was treated with aqueous emulsions of commercial SBR stabilizers (1.25 parts per 100 of polymer). The latex was creamed with varying proportions of 10 per cent sodium chloride solution and added to a well stirred solution of dilute sulfuric acid (at 60° C) containing a small amount of glue. The salt usage was equivalent to 0, 4, 8, 10, 15, and 19 parts per 100 parts of polymer. The acid and glue in each case was equivalent to 8 parts of 100 per cent sulfuric acid and 0.15 parts of glue per 100 parts of polymer. The resulting crumb slurry was stirred until the serum was clear. The serum was drained off and the flocculated crumb reslurried four times in fresh warm water. The polymer was squeezed to remove excess water, divided into small pieces by hand, and allowed to dry in a circulating air oven at 60° C for 16 to 20 hours. The dried crumb was massed on a cold mill and sheeted out
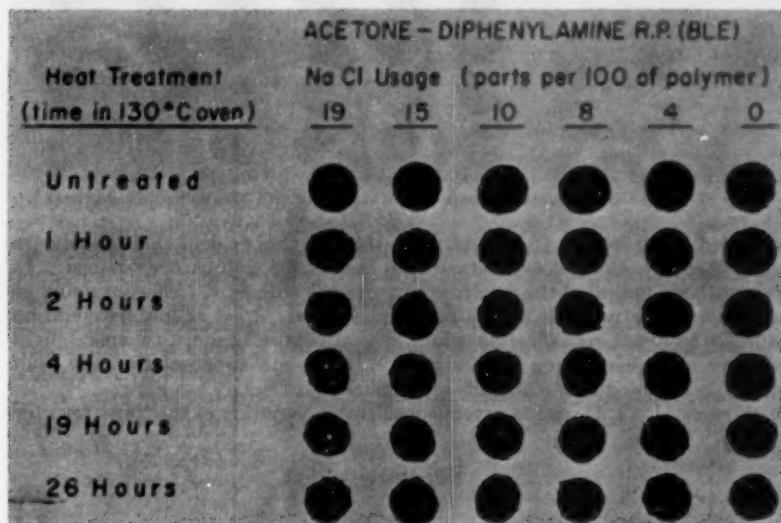

FIG. 14.—Effects of sodium chloride usage on heat stability of SBR 1503 (salt-acid flocculation).

to $\frac{3}{16}$ in thickness (after shrinkage). Portions were placed in a 130° C oven for varying periods of time. The effects of 130° C heat on the polymer stabilized with tris(nonylated aryl) phosphite and flocculated with varying amounts of salt are indicated in Figure 11.

The melted (shiny) appearance of the samples to the left and bottom of the chart reveals the poor heat stability of the polymer flocculated with the higher amounts of salt. It will be noted that as the quantity of salt employed in the flocculation of the latex is decreased, the time for resinification at the 130° C temperature increases. Those polymers flocculated with the higher amounts of salt show the poorest heat stability. Common usage of salt in commercial SBR production generally approaches the higher proportions indicated (15 to 20 parts per 100 of polymer).

Results of similar experiments with SBR 1503 stabilized with styrenated phenol, a higher alkylated phenol, and a diarylamine-type stabilizer (BLE) are

Fig. 15.—Effects of sodium chloride usage on heat stability of SBR 1503 (salt-acid flocculation).

indicated in Figures 12, 13, and 14 respectively. It is evident that the adverse effect of sodium chloride is observed with each of the stabilizers examined. In Figure 15 are indicated the results of experiments with SBR 1503 containing no stabilizer. The polymer in this case was carefully dried at low temperature (40° C) to avoid resinification which will otherwise occur with unstabilized polymer at higher drying temperatures. It is quite apparent that the "salt effect" is obtained in the absence of stabilizer.

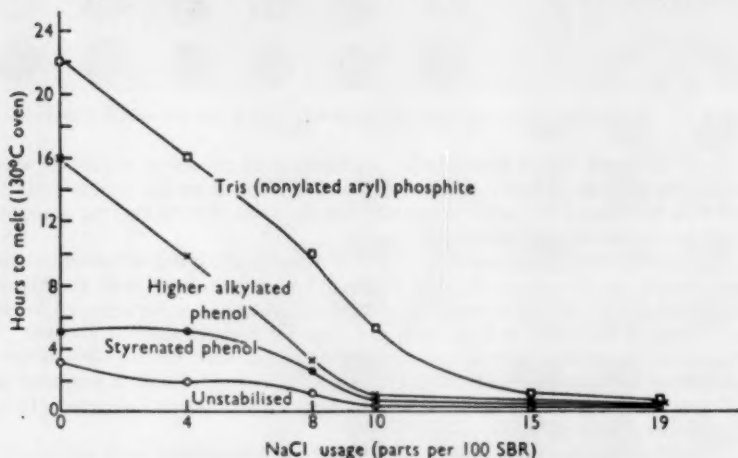Figures 11, 12, 13 and 14 reveal considerable variation in the times required

Fig. 16.—Relative effects of stabilizers on resinification of SBR 1503.

for resinification at any given salt level for the stabilizers tested. These differences are demonstrated graphically in Figure 16. The decreasing effectiveness of each of the stabilizers with increasing salt usage is very evident. Tris(nonylated aryl) phosphite gives most effective protection among the non-staining stabilizers. At high salt levels the efficiency of each of the materials reaches a low level.

It should be stated that differences between conditions of laboratory and commercial plant flocculations do not permit absolute comparisons to be made. Other studies have shown a greater advantage for the better stabilizers at the 15 to 20 parts of salt level than is indicated in Figure 16. On the other hand, it is well known that less effectively stabilized polymers are barely adequate in commercial production since special drying precautions are usually necessary to retain good color and freedom from resinification in such cases.

MECHANISM OF THE SALT EFFECT

The adverse effect of sodium chloride upon the heat stability of SBR polymer presents an interesting phenomenon. Among the suggestions that have been offered to explain the effect is the idea that salt may cause physical breakdown of the stabilizer emulsion and thereby prevent effective incorporation of the stabilizing agent in the polymer. This idea is not supported by the evidence given in Figure 15 which demonstrates that the salt effect is observed in the absence of stabilizers.

Another explanation considers that the improved stability of acid-glue flocculated polymer is due to traces of retained sulfuric acid. It is known that certain acidic substances such as acid esters of phosphoric acid exert a pronounced stabilizing effect on SBR polymer[22]. The effect of salt in salt-acid flocculation is visualized as involving the removal of residual sulfuric acid by interaction with traces of salt in the drying oven to produce volatile hydrogen chloride.

A more reasonable explanation has been offered by Reynolds[22] who has observed the deleterious effects of organic soluble iron compounds on oil ex-

Sodium Chloride
⟶ Cl ⟶ FeCl₃
Iron   Oxidation Caralyst
(Soluble in Polymer)
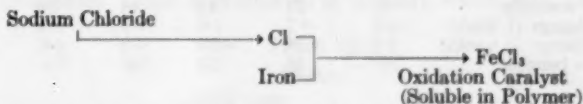
tended SBR polymer[21]. Reynolds points out that ferric chloride is among the salts of iron which have enhanced solubility in organic media. Chloride ion in salt-acid flocculation is visualized as solubilizing trace iron in the polymer and creating an effective oxidation catalyst.

This explanation is supported by experiments which have shown that other chloride salts including calcium chloride, magnesium chloride, and potassium chloride when employed as coflocculants in place of sodium chloride also produce poorly stabilized polymers whereas salts such as magnesium sulfate, sodium sulphate, and potassium sulfate give more stable polymers (see Figure 17).

EFFECTS OF POLYMER STABILITY ON QUALITY OF
SBR VULCANIZATES

Salt-acid vs. acid glue flocculation.—Two commercial "hot" SBR polymers, SBR-1000 (SYNPOL 1000, Texas-U. S. Chemical Company) and SBR-1007
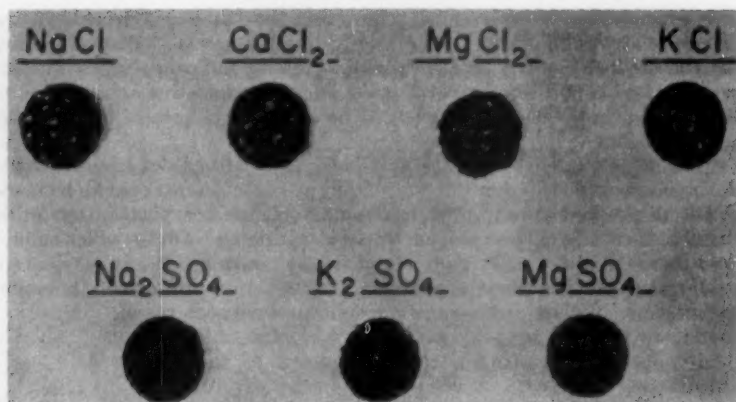
Fig. 17.—Effects of several salts as cofloccuants of SBR 1502.
(After 90 minutes in 130° C oven.)

(SYNPOL 1007, Texas–U. S. Chemical Company) were chosen as polymers identical in all respects except that SBR-1000 is flocculated with salt and acid and SBR-1007 is flocculated with acid and glue. The relative stability of the two polymers under two conditions of hot milling (15 minutes at 300° F and 15 minutes at 350° F) is revealed in Mooney viscosity and gel measurements on the

TABLE VI

EFFECTS OF FLOCCULATION METHOD ON THE STABILITY OF "HOT" SBR

Polymer Flocculation method	SBR-1000 Salt-acid			SBR-1007 Acid-glue		
		15 min	15 min		15 min	15 min
Hot milling treatment	None	300° F	350° F	None	300° F	350° F
Mooney viscosity	43	24	42	48	36	37
Points change (1 week)	+2	+7	+6	+1	+4	+2
Points change (4 weeks)	+2	+18	+20	+2	+6	+4
% Gel in benzene	Nil	36	32	Nil	Nil	Nil

milled polymers (Table VI). Less Mooney variation and better control of gel buildup are characteristic of the acid-glue flocculated polymer.

The polymers subjected to the conditions of milling described above were compounded and cured. The recipe employed is shown in Table VII.

The stocks were cured for 30, 60 and 90 minutes at 45 psi gauge steam pressure (292° F). The unaged physical properties of the vulcanizates cured for 60 minutes at 45 psi are shown in Table VIII.

TABLE VII

RECIPE

SBR-1000 (or 1007)	100.0
Protox 166	5.0
Wyex black	40.0
Sulfur	2.0
MBTS	1.75

Differences in the physical properties of the vulcanizates from polymers not subjected to hot milling are not great. In those vulcanizates from polymers subjected to 300° and 350° F milling, the effects of polymer stability become apparent. The retention of modulus, tensile, and elongation is definitely superior in the vulcanizates from the acid-glue flocculated polymer as compared to the vulcanizates from the salt-acid polymer. Similar advantages are seen in the cut growth properties of the acid-glue polymer. These data reflect the improved heat stability of the polymer flocculated without salt.

TABLE VIII

EFFECT OF FLOCCULATION METHOD ON POLYMER STABILITY AS REFLECTED
IN THE PHYSICAL PROPERTIES OF VULCANIZATES

Polymer Flocculation method		SBR-1000 Salt-acid			SBR-1007 Acid-glue	
		15 min.	15 min.		15 min.	15 min.
Hot milling treatment	None	300° F	350° F	None	30° F	350° F
Unaged physical properties (60 min/45 psi gage cure)						
300% Modulus (psi)	1070	1670	1330	930	890	930
Tensile (psi)	3100	2270	2070	2960	2890	2750
Elongation, %	590	380	420	620	620	600
Cut growth (0.001 in./kc.)	0.0	5.1	3.6	0.9	1.0	1.1

In experiments in which carbon black was added prior to the hot milling treatment to the two polymers described above (SBR 1000 and SBR 1007) the differences in the vulcanizates from the salt-acid and the acid-glue flocculated polymers were much less apparent than when the polymers were hot milled in the absence of the black[25].

BENEFITS OF STABILIZERS ON AGING OF VULCANIZATES

Effective stabilizers for SBR generally confer improved aging resistance on SBR vulcanizates. This is illustrated in a study where SBR 1502 polymer

TABLE IX

RECIPE

SBR 1502	100
Wyex black	40
Protox 166	5
Sulfur	2
MBTS	2

stabilized with several stabilizers was compounded, using normal mixing procedures, cured, and the resulting vulcanizates subjected to conventional aging tests.

Commercial SBR 1502 latex was obtained subsequent to the short-stopping and stripping operations but prior to the incorporation of the usual stabilizer. The latex was divided into several portions and treated with the three commercial stabilizers previously referred to. The stabilizers were added to the latex (1.25 parts per 100 of polymer) as emulsions and the latex flocculated, using the salt-acid technique. One portion of the latex was flocculated without stabilizer. The washed and dried polymers were compounded in a conventional SBR test recipe (Table IX) using normal milling procedure and cured at 292° F. The

vulcanizates were subjected to aging for 72 hours at 100° C and also for 96 hours in the oxygen bomb. Tensile values on the unaged vulcanizates (the data on the 60-minute cure were optimum) and on the aged samples are plotted in Figure 18. Best retention of tensile in the 100° C heat aging test was observed with stocks containing the acetone-diphenylamine reaction product and with tris(nonylated aryl) phosphite. The comparative antioxidant effectiveness of these materials was particularly evident in the oxygen bomb aging of the vulcanizates.
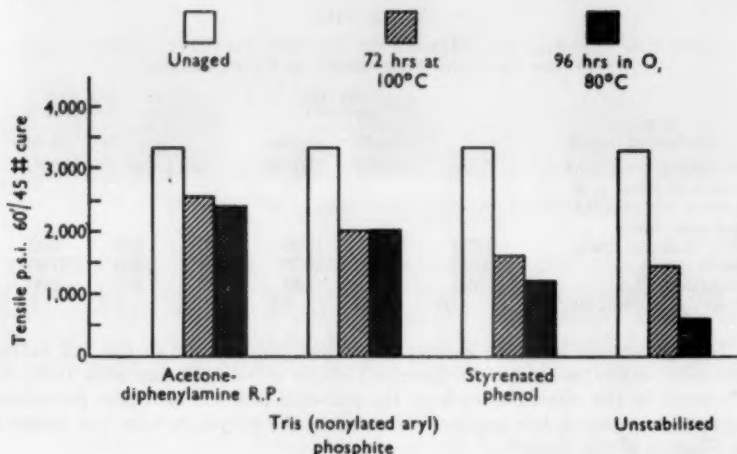

FIG. 18.—Tensile properties of aged vulcanizates from normally milled polymers. Influence of stabilizers as antioxidants.

CONCLUSIONS

(1) Styrene-butadiene rubber (SBR) is very susceptible to oxidative degradation unless an effective stabilizing agent is incorporated in the polymer during manufacture.

(2) Degradation of SBR appears as discoloration or resinification during drying of the polymer or during storage. Changes in the polymer may appear as variation in Mooney viscosity or as an increase in gel content.

(3) Deterioration of inadequately stabilized SBR may also show up during processing operations when the polymer is subjected to heat—as in the Banbury or on a hot mill.

(4) Deterioration of SBR polymer will appear as degraded physical properties in the cured vulcanizate.

(5) The rubber goods manufacturer will benefit from the use of a really effective SBR stabilizer incorporated in the polymer during manufacture or by adding additional stabilizer to provide more protection against heat degradation in his operations.

(6) Tris(nonylated aryl) phosphite exhibits unusual effectiveness as a stabilizer for SBR.

(7) The presently widely used method of salt-acid coagulation of SBR polymer leaves room for improvement as far as polymer stability is concerned.

(8) The more effective SBR stabilizers exhibit benefits in the aging of SBR vulcanizates.

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THE SORPTION OF ANTIOXIDANT
FROM SOLUTION *

E. N. Novikova

It is well known that both the nature of the adsorbent and the nature of the medium have an influence on the sorption of substances from solution. The character of the sorption isotherm is determined to a significant degree by the nature of the medium, which in various ways interacts with the molecules of the dissolved substance and by this, influences the character of the isotherm. The chemical nature and structure of the molecules of a dissolved substance is of great importance in the sorption of substances from one solvent or another.

A series of works[1, 2] has established the connection between the chemical nature of the adsorbate and the degree to which the adsorbate is sorbed. The dependence of the sorptability of a substance on the position and mutual influence of the occupied groups, which determines the polarity of the substance, was established[3, 4]; the influence of steric differences in the structure of the adsorbate on the degree of the sorption of that material from solution has been studied.

On the other hand, many investigators explain the protective actions of rubber antioxidants[6, 7, 8], mineral oil antioxidants[9] and antioxidants for other substances also by the chemical nature and structure of the inhibitor molecules and by the character and number of the functional groups which determine the relative polarity of the molecules containing them.

From this point of view it is of interest to determine if there exists a connection between the degree of sorption of inhibitors by rubber and the protective action of the inhibitors against the oxidation of rubber.

The problem is that of studying the relative sorption of the inhibitor in rubber, taking into account the chemical nature and structure of the inhibitor molecules, and also the polarity of the medium. Similar investigations are still important because they permit the study of the surface of the rubber, its porosity and the nature of the bonds with the inhibitor.

All of the present work consists of an investigation of the relative sorption of amines, hydroxy amines and naphthols from polar solvents by synthetic rubber.

EXPERIMENTAL

A styrene-butadiene rubber SKS-30 (SBR) and a polar rubber SKN-40 (NBR) that had been ground and screened through a mesh with 1 mm openings were used as adsorbents. The adsorbent was washed many times with acetone and methyl alcohol in order to remove resin and inhibitor (N-nitrophenyl-diazone was used to test for PBNA (phenyl-2-naphthylamine)), then dried in a vacuum to a constant weight. The inhibitors chosen for this investigation were those amines, hydroxy amines and naphthols which are used as antioxidants in rubber. All of the substances which were to be tested with rubber as the adsorbent were recrystallized or sublimed and the melting points checked.

The media from which sorption occurred were water and ethyl alcohol. In carrying out the experiments the contact method of sorption from solution was used. A 0.5 gram portion of synthetic rubber was mixed with 10 ml of a solution of a determined concentration (from 0.5 to 10 mM per liter of solution) of the specific inhibitor. The mixture was shaken for 30 minutes at room temperature. The solution was then decanted and the equilibrium concentration of the inhibitor was determined with a Tsais interferometer in the case of aqueous solutions and with a SF-4 spectrophotometer in the case of alcoholic solutions. Initially calibration curves were obtained for the starting solutions of each inhibitor from which were determined the inhibitor concentration in the solution after sorption. The amount of the material that was adsorbed was calculated in mM per gram of rubber from the change in the concentration of the solution before and after sorption.
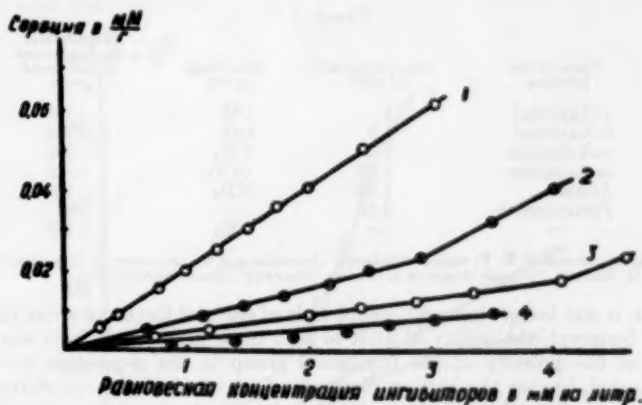

Fig. 1.—Sorption of inhibitor by SKS-30 from aqueous solutions (duration of sorption—30 minutes): 1—1-naphthylamine; 2—1-naphthol; 3—m-toluidine; 4—m-hydroxydiphenylamine.

SORPTION OF INHIBITORS IN SKS–30 FROM AQUEOUS SOLUTIONS

As may be seen from the data in Figure 1, substances which differ in chemical nature and structure are sorbed to a varying degree from water by the styrene-butadiene rubber (SBR). The degree of absorption of the 1-naphthylamine is significantly greater than the sorptability of 1- and 2-naphthols, a fact that might be explained by the different chemical nature and comparative electronegativity of the NH₂ and OH groups which are substituted on the naphthylene nucleus.

The magnitude of the sorption of 1-naphthol is greater than that of 2-naphthol which, evidently, is connected with the position of the hydroxy group which influences the polarity of the naphthol molecule. In the given case, a change in the position of the OH group has less influence on the magnitude of the absorption of naphthylene derivatives by the rubber than does the chemical nature of the NH₂-group.

The experiments showed that when the dipole moments of 1- and 2-naphthols were compared with the degree to which these inhibitors were sorbed from water by the SBR, the absorption of the naphthols decreased as their dipole moments increased (Figure 1, Table 1).

It should be noted that the values of absorption of *m*-toluidine and 2-naphthol were rather close, a fact which correlated closely with the dipole moments of their molecules. As may be seen in Figure 1, hydroxydiphenylamine was sorbed the least by the SBR.

Under the same experimental conditions, the ability of rubber to absorb *m*-anisidine, *m*-aminophenol, pyrocatechol, and aniline were investigated by us. This time, while *m*-toluidine was occluded to a certain degree by the SBR, *m*-anisidine, *m*-aminophenol, and pyrocatechol were not sorbed to a significant degree from water under the conditions of the experiment. The absence of sorption of *m*-anisidine, and *m*-aminophenol in comparison with the positive sorption of *m*-toluidine is a function of the structure of their molecules which contain the electronegative OCH_3 and OH groups, which are, in turn, characterized by relative high dipole moments (Table 1).

TABLE 1

Name of the inhibitor	Dipole moment* $M \times 10^{18}$	Functional group	Magnitude of dipole moment of functional group
1-Naphthol	1	OH	−1.6
2-Naphthol	1.3	OH	−1.6
m-Toluidine	1.27	CH_3	0.4
m-Anisidine	1.85	OCH_3	−1.2
Aniline	1.53	NH_2	1.5
Pyrocatechol	2.16	—	—
—	—	NO_2	−4.0

* Literature references: C. F. Smais, "Dielectric Constants and the Structure of Molecules", ONTI, 1937. L. M. Kulberg, "Organic Reagents in Organic Chemistry", Goskhimizdat, 1950.

Thus, it was found that with compounds of one and the same series (derivatives of benzene), the ability of SBR to sorb these compounds from water decreases as the polarity of the functional group in the *p*-position increases. Pyrocatechol, having the highest dipole moment of all of the adsorbates that were used, was remarkable in its inability to be absorbed from the polar solvent (water) by the rubber.

During the investigations on the sorption of antioxidants from an aqueous solvent, we were unable to establish in all cases a direct connection between the inhibitor action and the sorption of the active compound. One of the reasons for the difficulty encountered in establishing such a connection is the influence of the solvent and the varied nature of the materials being adsorbed.

In the investigations of various authors[10, 11] there has been shown a dependence of the adsorption on the polarity of the medium, namely: a higher value of molecular polarity of a solvent correlates with a smaller degree of adsorption of a polar molecule of a dissolved substance. Water, serving as the solvent in our experiments, is more polar than the rubber, SKS-30, which served as the adsorbent. If the medium is more polar than the adsorbent, the polar molecules of the inhibitors are able to hydrate or, in the general case, solvate which hampers their orientation with respect to the rubber and this shows up in the degree of sorption. Our experiments show a dependence of the degree of absorption of 1- and 2-naphthols, *m*-toluidine, and *m*-anisidine by the rubber on the magnitude of their dipole moments, bearing witness to the fact that sorption is influenced not only by the nature of the rubber but also by the polarity of the solvent.

Taking into account the fact[12] that the adsorption equilibrium of flexible structures is established slowly, we conducted a series of experiments to deter-

mine the sorption after 16 hours of contact of the adsorbent (rubber) with a solution of the appropriate inhibitor.

As is shown in Figure 2, the sorption equilibrium between the amount of inhibitor absorbed and the concentration of the inhibitor in solution is established slowly. The degree of sorption of the inhibitors is increased, although the order of their sorption activity is the same as that after 30 minutes of mixing the rubber with the solution. As for the quantity of inhibitor absorbed per gram of rubber, it is close to the concentration (1–2%) that is added to the rubber under factory conditions to protect it from oxidation.

In studying the dependence of the concentration of the original solution on the time of mixing of that solution with the rubber, it was found that the magnitude of the sorption per gram of rubber varied for 1-naphthylamine from 0.5 to 12 mg; for m-toluidine, from 0.5 to 4 mg, and for m-hydroxydiphenyl-amine, even less.
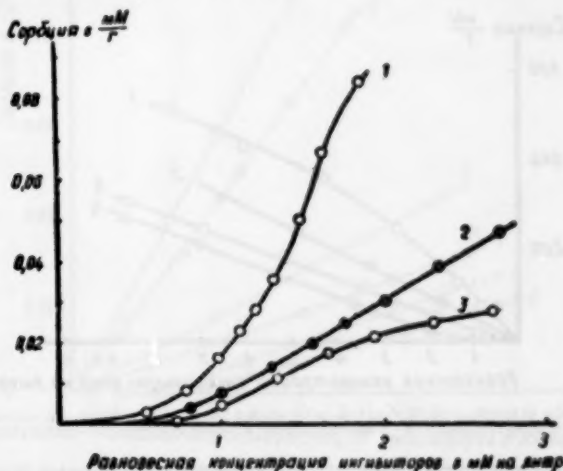
FIG. 2.—Sorption of inhibitor by SKS-30 from aqueous solutions (duration of sorption—16 hours): 1—1-naphthylamine; 2—1-naphthol; 3—2-naphthol.

Earlier[13] it was shown that the inhibitors studied by us, when ranked in order of their activity as an antioxidant for rubber, fall in the following series: 1-naphthylamine > 1-naphthylamine.

The magnitude of sorption of the same inhibitors from water on SBR lie in the reverse order: 1-naphthylamine > 1-naphthol > m-hydroxydiphenylamine. In contrast to m-toluidine, m-anisidine manifests a high antioxidant activity in rubber[14]. Contrarily, m-toluidine shows the highest magnitude of sorption on rubber.

SORPTION OF INHIBITORS BY SKN–40 FROM ALCOHOLIC SOLUTIONS

The sorption of inhibitors from absolute ethyl alcohol by the polar rubber SKN-40 was studied. The rubber was ground up and carefully washed with methyl alcohol in order to remove PBNA and other soluble ingredients.

The experimental method was the same as that in the previous experiments on sorption from aqueous solutions. The equilibrium concentration of the

inhibitors in solution after sorption was determined with the aid of a CF-4 spectrophotometer.

Beforehand, a calibration curve was obtained at distinct wave lengths in the visible and near ultraviolet regions for alcoholic solutions of each inhibitor. The light absorption was then determined on the decanted solution after sorption. The solution was placed in a cell with quartz windows and a thickness of 1 cm. The extinction was read directly from the dial of the spectrophotometer. The extinction is defined as $\log I_0/I$, where I_0 is the intensity of the light transmitted by the solvent and I is the intensity of the light transmitted by the solution in a cell of the same size. The equilibrium concentration of the inhibitor was determined from the change in the light absorption before and after sorption with the aid of the calibration curves. From the change in the concentration of the solution before and after sorption was calculated the amount of absorption of inhibitor in mM or in mg per gram of rubber.
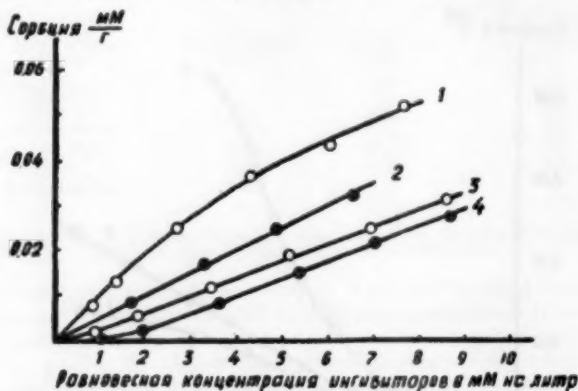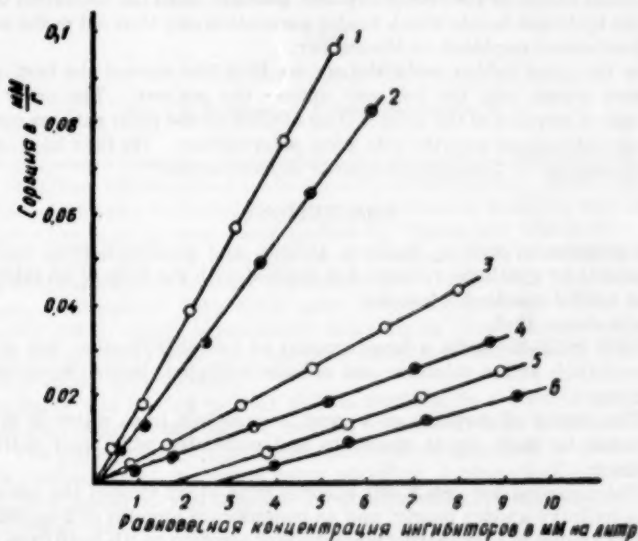

Fig. 3.—Sorption of inhibitor by SKN-40 from ethyl alcohol (duration of sorption—30 minutes): *1*—PBNA *2*—1-nitroso-2-naphthol; *3*—2-naphthylamine; 4—*m*-hydroxyphenyl-2-naphthylamine.

As is shown in our experimental data presented in Figures 3 and 4, substances which retard the oxidation of rubber are sorbed from ethyl alcohol by the polar rubber. The magnitude of the sorption increased linearly with the increase in the concentration of the inhibitor in the solution. It is possible to judge the degree of sorption of the various inhibitors from the angle the linear plots make with the axis of the abscissa. The amines phenyl-2-naphthylamine, 2-naphthylamine and diphenylamine were retained to a larger extent. To a lesser degree was absorbed the oxyamines *m*-hydroxydiphenylamine and *m*-hydroxyphenyl-2-naphthylamine with the latter being absorbed greater than the former.

The molecule of *m*-hydroxyphenyl-2-naphthylamine, in contrast to *m*-hydroxydiphenylamine, has a large hydrocarbon chain; consequently it must be solvated to a lesser extent by the alcohol and will be sorbed to a greater extent by the rubber. 2-Naphthol was sorbed to a quite insignificant degree. The comparatively small sorption activity of the oxyamines evidently is connected with the fact that they contain the polar, electronegative OH groups.

As is well known, the comparative electronegativity of the functional groups in the benzene nucleus has an influence on the symmetry of the distribution of the electrons around the nucleus and therefore on the polarity of the molecule.

The sorption of the hydroxy amines, as polar compounds, is complicated by the influence of the alcoholic solvent. As is the case in aqueous solvents, the polar molecules are able to form associations with the alcohol or solvate, which will decrease the degree of the sorption by the rubber.

The influence of the polar nature of the rubber on the absorption of the amines and hydroxy amines is not excluded. In conducting our preliminary experiments we were unable to detect a significant absorption of phenyl-2-naphthylamine and 1-nitroso-2-naphthol from ethyl alcohol by pale crepe or the SBR polymer SKS-30. But the same amines, as is indicated in Figures 3 and 4, are sorbed by the polar rubber SKN-40 from alcohol.

Fig. 4.—Sorption of inhibitor by SKN-40 from ethyl alcohol (duration of sorption—16 hours): 1—1-nitroso-2-naphthol; 2—PBNA; 3—2-naphthylamine; 4—diphenylamine; 5—m-hydroxydiphenylamine; 6—2-naphthol.

Thusly, polar rubber absorbs less of the polar inhibitors (amines) from the polar solvent while under the same experimental conditions natural and butadiene-styrene rubbers do not sorb these inhibitors.

As is seen in Figures 1-4, the adsorption isotherms are linear. A similar form of an isotherm follows from the use of the Langmuir adsorption equation $\Gamma = \Gamma_\infty(C/K + C)$, where Γ is the adsorption under equilibrium conditions; Γ_∞ is the adsorption under conditions of surface saturation; C is the equilibrium concentration; K is a constant.

Actually, if it happens that the value of C in the Langmuir equation in solutions of a minimum concentration may be neglected, and in our case we must work with solutions of a minimum concentration due to the difficult solubility of the inhibitor, the equation takes the form $\Gamma = (\Gamma_\infty/K)C$.

Since Γ_∞/K is a constant, it follows that the adsorption under equilibrium conditions (Γ) will be proportional to the given original concentration and in such a case the adsorption isotherm would be linear.

The degree of sorption of amines by the polar rubber is extremely varied.

The amine that was absorbed the greatest was PBNA which is widely used in industry to protect rubber from oxidation. The magnitude of the sorption of the PBNA varied as a function of the initial concentration of the solution from 1.3 to 18 mg per gram of rubber.

Although 2-naphthylamine has a less complex molecule, it is absorbed by the rubber two times less than PBNA. At the same solution concentrations the sorption of the 2-naphthylamine varied from 0.8 to 6 mg. Diphenylamine exhibited an even smaller amount of sorption. 2-Nitroso-naphthol, in contrast to 2-naphthol, had a high sorbability by the rubber being very near to that of PBNA (from 0.8 to 16 mg). This is apparently connected with the influence of the chemical nature of the NO_2 group and, possibly, with the formation of intramolecular hydrogen bonds which hinder association and thus aid in the sorption of the 1-nitroso-2-naphthol on the rubber.

Thus the polar rubber sorbs the amines from the alcohol the best, as does SBR from water, and the hydroxy amines the poorest. The order of the magnitude of sorption of the amines from alcohol by the polar rubbers correlates with their antioxidant activity with a less polar rubber. We then have: phenyl-2-naphthylamine > 2-naphthylamine > diphenylamine[15].

CONCLUSIONS

The sorption of amines, hydroxy amines, and naphthols from water and ethyl alcohol by synthetic rubbers was studied with the help of an interferometer and a SF-4 spectrophotometer.

It was shown that:

1. SBR (SKS-30) sorbs a large amount of 1-naphthylamine, less of the 1- and 2-naphthols and m-toluidine and m-hydroxydiphenylamine to an insignificant degree.

2. The degree of sorption of 1- and 2-naphthols from water is inversely proportional to their dipole moments and correlates with their activity as antioxidants.

3. The polar rubber (SKN-40) absorbs from ethyl alcohol the amines the best, the hydroxy amines poorly, and an insignificant amount of 2-naphthol.

4. The amines in a decreasing magnitude of sorption on SKN-40 from alcohol fall in a series (phenyl-2-naphtholamine > 2-naphthylamine > diphenylamine) which correlates with their activity as antioxidants.

5. The electronegative OH group, sticking out of the body of the molecule, exerts an influence on the degree of sorption of m-hydroxyphenyl-2-naphthylamine, m-hydroxydiphenylamine and naphthol from polar solvents.

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FACTORS INFLUENCING THE STABILITY
OF SBR LATEX *

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The purpose of this research program has been the establishment and investigation of factors which influence the stability of SBR latex. Since high shearing forces are known to destabilize latex, a mechanical stability test based on this factor has been proposed and applied by Maron and Ulevitch[2]. In contrast, the study reported here has been conerned with the nonmechanical factors which contribute to latex destabilization. Little work has been done in this area, particularly with SBR latex (styrene-butadiene latex, formerly designated GR-S) which is inherently more stable than the natural product. Some of the extensive work that has been completed with natural latex served as a guide in the present study[4].

The study was limited to latex as it is produced in a polymerization plant for later conversion to dry rubber, and did not include latex destined for use as such. The approach to the problem has involved attempts to determine the various factors which influence latex stability, systematically study these factors, and assess in quantitative or semiquantitative fashion the relative importance of each factor.

PREPARATION OF LATEX

An SBR-1500 recipe was employed in the investigation of latex stability. The formulation includes a rosin-acid soap and a sugar-free iron-redox activator (Table I).

Polymerization was carried out in 32-ounce soda bottles in a tumbler-type (42 rpm) polymerizer at 5° C. This polymerizer was equipped to handle eight bottles. Reaction time began with the addition of an aqueous mixture of ferrous sulfate and potassium pyrophosphate to the bottle and was terminated with the addition of a shortstop (potassium dimethyl dithiocarbamate). A 20 per cent solids latex was prepared, on the average, in 4.5 to 5.0 hours. This corresponded to approximately 58 per cent monomer conversion. However, in some cases, the polymerization rate varied considerably from this average. Although unreacted butadiene was normally removed from the latex, no attempts were made to remove excess styrene. Polymerization time and solids content for the various latexes referred to in the text are listed in Table II.

TABLE I

THE SBR–1500 RECIPE

Ingredient	Parts by weight
Butadiene	70.0
Styrene	30.0
p-Menthanehydroperoxide	0.08
FeSO$_4$·7H$_2$O	0.16
Potassium pyrophosphate	0.19
Tetrasodium salt of ethylenediaminetetraacetic acid	0.01
Potassium soap of disproportionated rosin acid	4.50
Sodium salt of aryl sulfonic acid	0.15
Na$_3$PO$_4$·12H$_2$O	0.5
Tertiary dodecyl mercaptan	0.18
Water	200.0
Potassium dimethyl dithiocarbamate	0.2

STABILITY TESTS

Latex stability is of considerable practical importance.   Coagulation during manufacture may result in a considerable loss of operating time in addition to waste of raw material.   Additional problems result from coagulation during storage and shipment.   Maron and Ulevitch have shown that synthetic latex is considerably more stable than natural latex.

In the present study, the primary technique used in the determination of latex stability involved weight measurements of gross coagulum formed in the latex.   Before collecting the coagulum, the latex was stirred to redisperse any "cream" associated with the coagulum.   The coagulum was then removed from the surface of the latex with a spatula, placed in an aluminum dish, rinsed with distilled water, and dried at 60° C.

The second method used for following instability involved particle-size-distribution measurements.   A series of Millipore filters of graded pore size was used in this work.   The pore sizes of these filters are listed in Table III. The VM filter was used infrequently because of long filtration-time requirements.

The following procedure was adopted for particle size distribution measurements.   A dilute solution of latex, the concentration of which was chosen by trial and error, was filtered with suction through a Type AA Millipore filter. This filtration removed dust and small particles of coagulum.   It was then passed consecutively through weighed HA, PH, VC, and, if feasible, VM filters.

TABLE II

POLYMERIZATION DATA

Latex no.	Polymerization time, hr	Solids, %
43	3.33	16.7
55	2.08	13.6
59	4.83	21.7
60	5.33	22.4
62	5.00	20.6
63	4.75	22.9
64	5.17	22.2
65	4.75	24.1
66	4.75	24.1
67	4.75	29.1

TABLE III

PORE-SIZE DATA ON SEVERAL MILLIPORE FILTERS[a]

Code	Pore-diameter, microns	Pore-diameter variation, microns
VM	0.050	±0.003
VC	0.100	±0.008
PH	0.30	±0.02
HA	0.45	±0.02
AA	0.80	±0.05

[a] Millipore Filter Corp., Watertown, Mass.

These filters had been stored under desiccation at least 12 hours previous to weighing. The filters were then reweighed after being dried 12 to 24 hours at 40° C and redesiccated for 12 hours. From the amount of material retained by the various Millipore filters and the volumes of solutions filtered, particle-size-distribution data could be obtained. In such experiments, extreme care was exercised both in cleaning the filtration equipment and in handling the filters to avoid contamination with dust particles.

For routine experiments, measured volumes of latex were stored in one-pint wide-mouthed glass jars. Normally, a screw cap containing a venting hole ½ inch in diameter was placed on each jar. However, in many cases, variations of the venting conditions were employed.

Effect of temperature.—In an examination of the effect of temperature on the stability of SBR latex, 300-ml samples of the undiluted latex were stored in vented containers at room temperature and at 50° C. During storage at the higher temperature, the samples were stirred occasionally to reduce creaming. Representative results obtained in this study are given in Figure 1. The
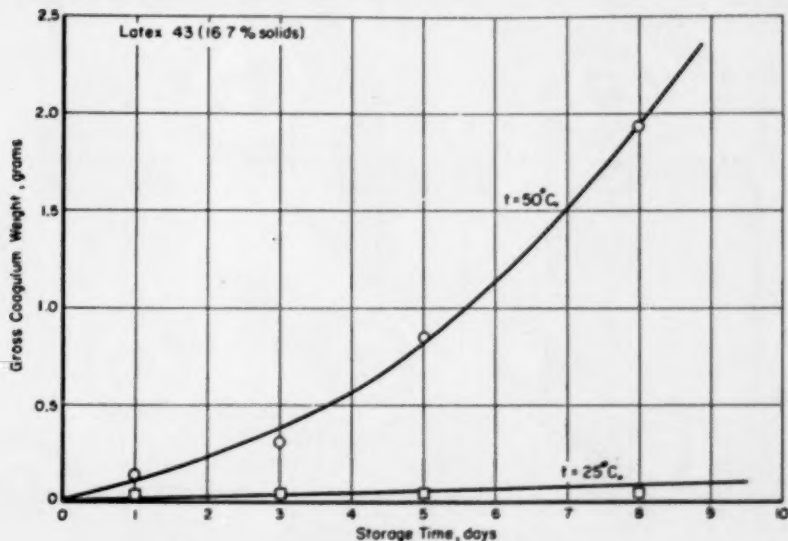
FIG. 1.—Effect of temperature on gross coagulum formation.
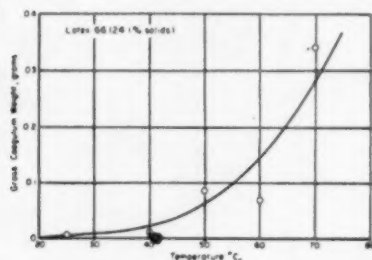
FIG. 2.—Effect of temperature on coagulum formation during
65 hours' storage under reflux.

coagulum weights plotted are cumulative. These results indicate that the
latex is quite stable at 25° C and definite destabilization occurs at 50° C.

The results from an additional study of the effect of temperature on latex
destabilization are illustrated in Figure 2.   In this study, equal volumes of the
latex were stored beneath a reflux condenser for 65 hours at the chosen tem-
peratures.   This test arrangement avoided any over-all loss of water, but did
not prevent local dehydration by water evaporation.   In this way, measur-
able quantities of coagulum were formed without gross concentration changes
occurring.

Effect of polymer concentration.—The effect on stability of stopping poly-
merization at a lower conversion than usual can be seen from a comparison of
the results obtained with latexes 55 and 60 (Figure 3).   From this experiment,
a 250-ml portion of each latex was stored in a vented container at 50° C.
Latex 60, containing 22.4 per cent solids, was prepared from the standard recipe
in 5.33 hours.   Latex 55 was obtained by withdrawing a portion of the latex
after 2.08 hours.   This latex contained 13.6 per cent solids.
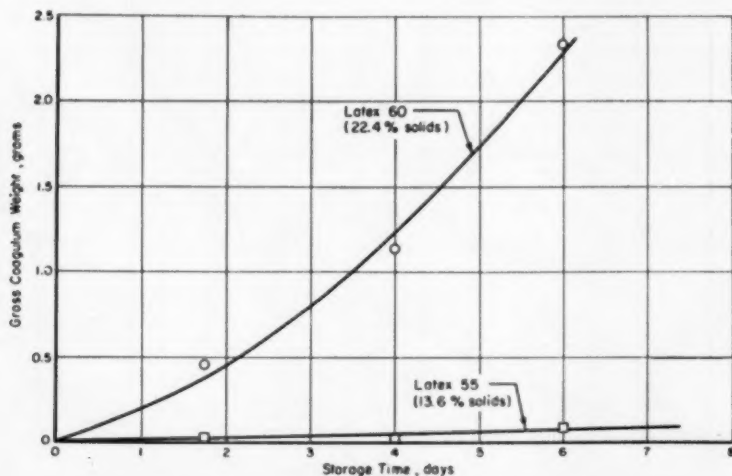
FIG. 3.—Effect of polymer concentration on gross coagulum formation at 50° C.
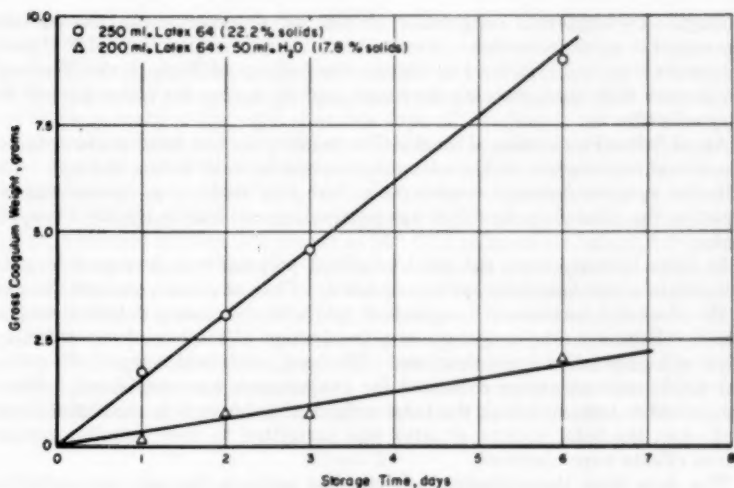
Fig. 4.—Effect of polymer concentration on gross coagulum formation at 25° C.

In order to determine whether the observed difference in stability between latexes 55 and 60 was solely a polymer concentration effect or was due to some other factor—e.g., molecular weight—several tests were conducted in which preformed latex was diluted with distilled water. The data (Figures 4 and 5) establish conclusively that polymer concentration, per se, influences latex
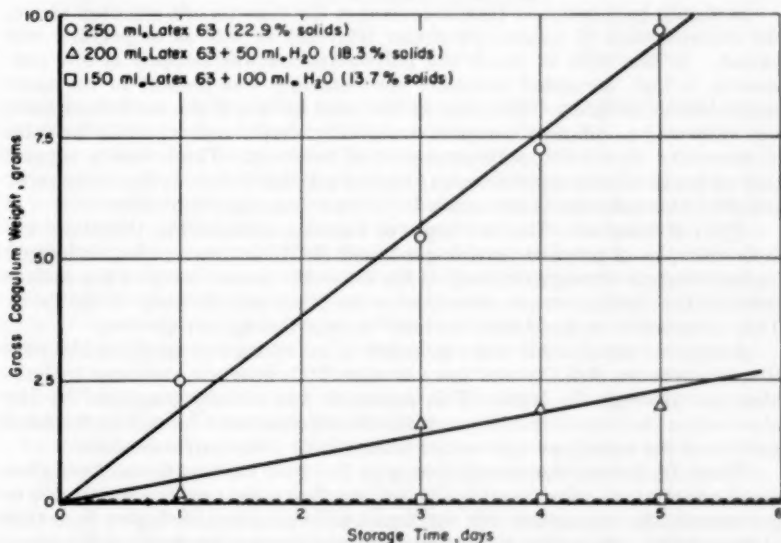
Fig. 5.—Effect of polymer concentration on gross coagulum formation at 70° C.

stability.   To accelerate coagulation in the 25° C experiments, the samples were stored in open containers.   Vented containers were used in the 70° C tests. The results reported here tend to confirm the findings of Ramage and Tierney[3], who showed that latex stability decreases rapidly during the latter part of the polymerization.

An additional indication of the relative stability of these latexes was obtained from visual observation of the amount of cream formed during storage.   The undiluted samples creamed considerably, but very little or no cream was observed on the diluted ones.   This was particularly evident in the 25° C experiments.

In these investigations the total weight of polymer was decreased in order to maintain a constant total volume of latex.   This, of course, accounts in part for the observed decrease in coagulation rate with decreasing polymer concentration.   However, the coagulum as a percentage of total solids is still much higher at higher solids concentrations.   Obviously, this is also true if the actual final solids concentrations corrected for evaporation was considered.   Moreover, in other tests in which the total weight of polymer was maintained constant—i.e., the total volume of latex was permitted to vary—similar concentration effects were observed.

The data from these studies indicate that perhaps the soap concentration is not as important a factor in stability as had been believed previously.   In diluting the latex with distilled water, some decrease in the concentration of soap bound to the polymer particles should occur so as to maintain the equilibrium between free and bound soap.   However, even with this decrease, stability has increased.   It is probable that, under the conditions of these experiments, particle collisions, the number of which decrease with dilution, are a more important factor in latex stability than soap coverage of polymer particle surface.

It should be mentioned that in several of the experiments reported above, the concentration of residual monomer (styrene) as well as of polymer was varied.   In the work in which the polymerization was stopped at low conversion, a high unreacted monomer concentration was present in the more stable low-solids latex.   However, in the work in which the preformed latex was subjected to dilution, increases in stability were observed, while the ratio of unreacted styrene to polymer remained constant.   These results suggest that although residual styrene concentration may have some influence on latex stability, this influence is secondary to polymer concentration effects.

Effect of interface.—The two types of interface examined in this study are both examples of polymer particle-gas-liquid (PGL) interface.   One is formed by bubbling gas through the body of the latex; the second involves the surface between the continuous gas phase above the latex and the body of the latex. This connotation of the world "surface" is used throughout the test.

A series of experiments was conducted in an attempt to establish the relationship between stability and the extensive PGL interface produced by bubbling gas through the latex.   This approach was initially suggested by the observation that considerable quantities of coagulum were formed on the latex surface as the butadiene was vented immediately after polymerization.

When dry helium was passed through a No. 30-C Corning borosilicate glass gas-dispersion tube into a sample of latex, at a flow rate of approximately 100 cc per minute, the coagulation rate was found to be considerably higher than that of the control.   However, in bubbling dry gas through the body of the latex, considerable dehydration occurred and the solids content increased from 29.1

to 43.1 per cent during a 5-day test at 50° C.   In order to reduce concentration effects in later work, the helium was first saturated with water by passage successively through columns of water at 60° and at 50° C.   In these tests, using the same flow rate of gas, no coagulum was formed at 50° C in 1.75 days. These findings make it apparent that this type of interface is not effective, per se, in promoting latex destabilization.   This is in agreement with the work of Maron[1] who has stated that bubbling of gases through the latex does not result in coagulation, provided that evaporation of water from the latex is prevented.

In attempting to relate the second type of interface—i.e., latex surface—to stability, a sample of latex was stored at 50° C in an open container, 5.9 grams of coagulum were formed in 0.75 day.   In a similar experiment in which the surface of the latex was covered with a layer of xylene, coagulation was completely retarded for periods exceeding 2 weeks.   These results indicate that coagulation can be prohibited by restricting evaporation from the latex surface. They further suggest that a localized dehydration of the polymer particles near the surface may promote coagulation.   Localized dehydration can be distinguished from over-all dehydration, such as occurs when a latex is concentrated,

TABLE IV

EFFECT OF SURFACE AREA AND AGITATION ON
GROSS COAGULUM FORMATION AT 25° C

	Latex No.			
	62-7	62-8	62-9	62-10
		Surface Area, Sq. Cm.		
	58	50	38	38
		Agitation		
Storage time, days	None	None	None	Mild
		Total coagulum formed, grams		
1.0	1.1	0.6	0.5	Negligible
2.0	8.0	5.5	3.6	Negligible
3.0	16.0	11.5	6.7	Negligible

in that the degree of dehydration is not uniform for all the particles in the latex. Returning to Figure 2, where the latex was stored under reflux, no increase in polymer concentration occurred during prolonged storage at 50° C.   However, a considerable amount of coagulation took place, indicating that localized polymer particle dehydration promotes destabilization even in the absence of over-all concentration of the latex.   Such a mechanism would also account for the increase in stability observed when the latex is diluted with water.   If destabilization occurs through a dehydration mechanism, it is probable that creaming is a substage in the dehydration because, in general, creaming and coagulation appear to be associated.   A logical sequence of steps in the destabilization process would be (1) particle growth, (2) creaming under the influence of gravity, and (3) coagulation under the influence of evaporation.   Polymer concentration would have a positive effect on each of these steps.   Temperature would affect steps (1) and (3) in a positive manner.

To relate latex surface and stability further, a study was conducted in which equal volumes of latex were stored in open containers and the area of the surface was varied.   These results, shown in Table IV, not only illustrate the importance of surface in latex destabilization, but also impose the added restriction that the surface must remain static for coagulation to occur.   This again is indicative of a localized polymer-particle dehydration.   Moreover, the solids

content of the agitated sample (62 to 10) increased from 20.6 to 36.6 per cent without coagulation taking place, showing that static surface is an important factor in latex destabilization. This concept that surface agitation retards destabilization has been verified by additional experiments.

To ascertain the mechanism of destabilization further, an experiment was carried out in which the effect on stability of the water vapor concentration in the gas phase above the latex was examined. If a localized polymer-particle dehydration forms the basis of the destabilization mechanism, a water-saturated gas phase in contact with the latex surface should, in the presence of a static

TABLE V

EFFECT OF GASEOUS HEAD SPACE ON COAGULUM FORMATION

Latex no.	Container	Temp., °C	Storage time, days	Gaseous head space	Coagulum, grams
67-6	Open	25	3.0	Dry	2.03
67-7	Sealed	25	3.0	—	Negligible
65-1	Open	60	1.0	Dry	3.38
65-2	Open	60	1.0	Water saturated at 60° C	Negligible

surface, prohibit dehydration and, consequently, render the latex stable. This postulate has been verified by the data presented in Table V.

It should be mentioned here that, in the majority of the experiments described in this work, the formation of cream was observed to precede coagulation. As stated previously, this is believed to be the first of two time-dependent dehydration stages in the destabilization process. In this stage, the formation of more or less reversible aggregates takes place. It is accompanied by an increase in viscosity. When this cream is further dehydrated, the irreversible process of coalescence occurs.

TABLE VI

CHANGES IN PARTICLE SIZE DISTRIBUTION IN SBR
LATEXES DURING STORAGE AT 50° C

	Latex no.			
	55C	55C	59C	59C
		Storage time, days		
	2.0	8.0	2.0	8.0
		Solids, %		
Particle size range, microns	13.6	18.2	21.7	25.7
		Weight, % of particles		
>0.45	<1.0	<2.0	<1.0	—
0.10–0.45	0.0	50.0	4.0	~100
<0.10 (by difference)	>99.0	>48.0	>96.0	0

To summarize, briefly, the effect on latex stability of the two types of interface examined, we can say that:

1. PGL interface, per se, is ineffective in promoting latex destabilization. The interface produced by bubbling gas through the body of the latex does not directly affect stability.

2. One form of PGL interface, surface, is associated with destabilization. A static latex surface in contact with an unsaturated gas, a condition that is favorable for localized dehydration, contributes to relatively rapid coagulum formation.

RELATIONSHIP OF STABILITY AND LATEX PARTICLE SIZE

In an examination of the relationship of stability and latex particle size, particle-size-distribution data were obtained for latexes 55 and 59 after 2 and 8 days' storage in vented containers at 50° C. The stability behavior of these latexes was typical—i.e., the higher solids latex coagulated at a much greater rate. For the particle-size-distribution measurements, dilute solutions of latex (0.1 ml of latex diluted to 1 liter) were filtered with suction through the series of graded Millipore filters described earlier. The data from this study are listed in Table VI.

The results of these experiments show a very marked increase in weight-average particle size during storage and, consequently, during destabilization. Further, the particles of the high-solids latex grew more rapidly than did those of the low-solids latex, although only a small percentage of particles were found in the > 0.45-micron size range. These data are best explained by assuming

TABLE VII

EFFECT OF INITIAL PARTICLE SIZE DISTRIBUTION ON
GROSS COAGULUM FORMATION AT 50° C

	Latex no.	
	67-4	67-5
	Weight, % of particles in micron range	
	>0.45-0	0
	0.10-0.45- <20.0	~100
	<0.10- >80.0	0
Storage time, days	Total coagulum formed, grams	
2.0	0.19	3.56
5.0	0.83	7.72

that all the particles grow during the destabilization process with the larger ones coagulating. Further, the fact that the latex with larger particles coagulates more readily supports the idea that the amount of particle surface covered by soap is not so important a factor in stability as was previously believed.

To show the relationship between coagulum formation and particle size more clearly, two samples of nearly equal solids content, but of considerably different particle-size distributions were employed. One latex sample had been subjected to elevated-temperature destabilization for a 24-hour period previous to the start of these tests to obtain larger particle sizes. The results of this study are reported in Table VII.

This study affords additional evidence that the larger particles are the ones associated with the ultimate destabilization process. These results in combination with the data of Table VI support the theory that all the particles of the latex grow during destabilization. This means that some particle-size growth occurs that does not lead immediately to formation of coagulum. That is, the formation of coagulum is more of a condensation process than a chain-growth process. It is possible, however, that chain growth occurs above some critical particle size. This might account for the almost complete absence of particles in the > 0.45-micron size range.

SUMMARY

The theory is proposed as a result of this work that under "static" conditions, latex destabilization proceeds through a time-dependent localized polymer-particle dehydration. This dehydration apparently occurs in two stages.

In the initial stage more or less reversible aggregates are formed. This creaming is accompanied by a perceptible increase in viscosity. In the second stage the aggregates are further dehydrated and coalescence occurs. This latter process is irreversible.

Evidence is presented to support the argument that the prime requirement for the dehydration and, consequently, for the destabilization of high-stability latex is the presence of a static latex surface in contact with an unsaturated gas phase. Three factors involved here are (1) surface area, (2) surface agitation, and (3) the degree of saturation of the gas phase in contact with the surface. In addition, it is shown that particle growth precedes the destabilization and that stability is influenced by a number of other factors, including (1) temperature, (2) polymer concentration, and (3) polymer-particle size, which contribute, either directly or indirectly, to the dehydration process.

ACKNOWLEDGMENT

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PHYSICAL CHEMICAL FACTORS IN BOND STRENGTH IN MULTIPLY VULCANIZED ARTICLES *

B. A. DOGADKIN

Bond strength between the components of multiply articles in the vulcanized state depends on many factors which make themselves evident in the various stages of manufacture of the articles as well as under service conditions. In the present paper we shall give a description of the main physical chemical factors which were revealed in the course of experimental work in the physics and chemistry divisions of the Tire Research Institute, mainly in 1951 to 1953.

CHANGES IN THE SURFACE LAYER OF CALENDERED SHEETS DURING STORAGE

We usually ply up compounded stocks as they come from the calender (or the extruder). The surface layer of such stocks immediately after issuing from the calender hardly differs in composition and structure from the properties of the stock in the bulk. The likelihood of orientation and other phenomena in the surface layer is reduced by the high viscosity of the system. Therefore in plying-up vulcanized rubber sheets of one and the same composition which have only just come from the calender, at temperatures considerably exceeding the glass temperature (which practically always takes place in rubber technology) we have the necessary conditions for their autohesion ('samoslipanie') through diffusion of the molecular chains of the raw rubber from one layer into another and the disappearance of the boundary layer (Figure 1). After the diffusion process has taken place the contact layer will possess the properties of the material in the bulk, in particular the tensile strength which is characteristic of the material itself.

The duration, and consequently the completeness of the process of autohesion depends, as we shall show below, upon the temperature, the pressure and other factors. The presence of air absorbed on the pliedup surfaces cannot have any real adverse significance in respect to the bond strength of fresh surfaces of a single material, since the adsorbed air rapidly diffuses into the thickness of pliedup layers.

The picture is completely changed, if the layer of rubber is stored for some time prior to plying up. In this case there take place gradually in the surface layer chemical and structural changes which may have an adverse influence both upon the tackiness of the stocks and upon the bond strength between them in the vulcanized state.

We observe here two groups of phenomena: (1) the diffusion phenomena of blooming to the surface of the low molecular components of the stock (sulfur, accelerators, softeners etc.) and (2) irreversible alterations connected mainly with the action of the oxygen in the air.

We determined the alterations in the surface layer of the vulcanized rubbers during storage from the alteration in the surface resistivity, from the

alteration in the microrelief of the surface, and from the alteration in the character and intensity of luminescence of the surface in ultraviolet light. Thus the surface resistivity of calendered sheets of a breaker stock increases after 24 hr storage from 2×10^{10} to 4×10^{10} ohm-cm. The alteration in the microrelief of the stock is distinctly noticeable on studying the surface in reflected light in a binocular microscope (Figure 2). (Figure 2 is not reproduced in this translation, owing to the poor quality of the photograph). The alteration in the character of the luminescence is connected fundamentally with oxidation of the surface of the rubber[1].
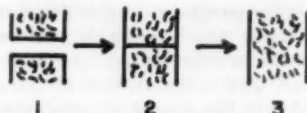
FIG. 1.—Disappearance of boundary layer: 1, before plying-up; 2, diffusion in pliedup state; 3, disappearance of boundary layer as result of autohesion.

The first group of phenomena—diffusion of compounding ingredients to the surface—is of essential importance in relation to the tackiness of the stocks in the raw state in building up articles, but obviously plays a lesser role in relation to the bond strength in the vulcanized state. Where the pliedup layers are in contact with each other for a sufficiently long period before the moment of full cure, bloom on the surface of the material diffuses in the reverse direction into the thickness of the plies, the concentration gradually equalizing itself in the entire volume of the rubber. Therefore the adverse influence of blooming of compounding ingradients upon the bond strength in the vulcanized state will become apparent only if before the moment of formation of the vulcanization network no migration of these ingredients takes place from the contact zone into the thickness of the rubber.

TABLE 1

INFLUENCE OF STORAGE OF SPECIMENS IN AIR UPON BOND
STRENGTH IN THE VULCANIZED STATE

Time of storage before plying up, hr	Bond strength, kg/cm	Percentage of specimens undergoing separation at the joint
1	—	0
4	6.4	25
8	6.0	50
24	4.6	100
48	5.0	100

The second group of phenomena, connected with the interaction of the surface with the oxygen of the air, leads to irreversible changes in the composition and structure of the material and thus may have an adverse effect both on the process of autohesion and upon the bond strength in the vulcanized state.

This was shown by experiments in the preparation and storage of sheets of tread and breaker stocks of SKS-30 (SBR) in air and in a nitrogen atmosphere. While storage in nitrogen for 48 hr practically did not alter the bonds trength, storage in air (removing any possible dust) led to a gradual fall off in the bond strength and an increase in the number of specimens undergoing ply separation in static tests (Table 1). This fall off in bond strength is apparently explained

TABLE 2

INFLUENCE OF SUBSTANCES WITH VARIOUS FUNCTIONAL GROUPS UPON
THE BOND STRENGTH OF PLIEDUP RUBBERS (TREAD
SKS-30A, BREAKER SKB)

Substance used	Strength in static separation, kg/cm		Type of separation
	20°	100°	
Without treatment	6.9	1.5	50% in the rubber 50% in the joint
5% solution of benzoic acid	10.5	3.4	75% in the rubber 25% in the joint
5% solution of benzoyl peroxide	9.6	3.1	Same
5% solution of benzaldehyde	7.8	1.8	50% in the rubber 50% in the joint
5% solution of diproxide	7.0	1.2	Same
5% solution of trichlorothiophenol	6.9	1.5	Same
5% solution of piperidine	5.4	1.2	In the joint
5% solution of N,N'-di-phenyl-p-phenylenediamine	6.2	1.4	In the joint

by the fact that as a result of interaction with the oxygen there is formed a surface layer of oxidized and structurized rubber, which on the one hand prevents the diffusion process of autohesion, and on the other has an adverse influence both during vulcanization and in the fatigue of the boundary layer in the article.

It might be supposed that the application to the surface of the rubber of various substances which retard oxidation and structurization of the raw rubber protects the surface layer from interaction with the oxygen and thus assists enhancement of the bond strength. We tested a series of substances with various functional groups, including a series of active antioxidants (Tonox, Oxinone, N,N'-Diphenyl-p-phenylenediamine etc.). Only three of these substances gave a positive effect (Table 2).

The lack of a significant advantageous effect from the use of these substances is explained apparently by the fact that in mechanical processing (on the mill or the calender or in the extruder) there are formed allyl radicals, while in the case of synthetic rubbers containing a large number of 1,2 structures, alkyl groups are formed as well, which interact very vigorously with the oxygen in the air according to the scheme

$$-CH_2-CH=CH-CH_2-CH_2-CH=CH-CH_2- \xrightarrow{\text{Mechanical chain scission}}$$

$$\longrightarrow -CH_2-CH=CH-CH_2- \xrightarrow{+O_2} -CH_2-CH=CH-CH_2-O-\dot{O}\longrightarrow$$

$$\longrightarrow -CH_2-CH=CH-CH_2- \longrightarrow -CH_2-CH-\dot{C}H-CH_2-$$

$$\begin{array}{c} | \\ O \\ | \\ O \\ | \\ CH_2 \\ | \\ CH \\ || \\ CH \\ | \\ CH_3 \end{array}$$
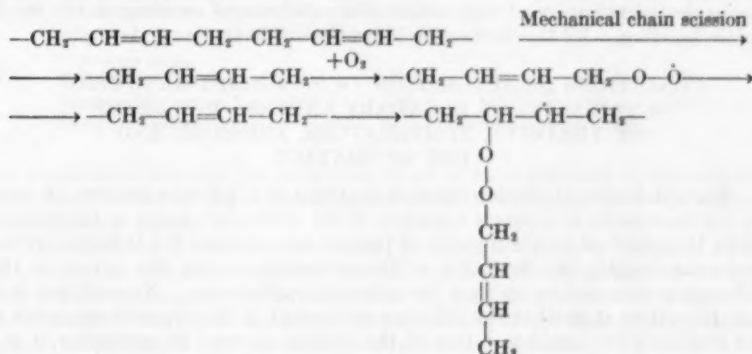
In this we show only one of the possible types of oxygen action upon the structure of rubber; this action leads to the setting up of a spatial network, and consequently to the loss of the plastic properties of the rubber. In other words, as a result of such a process there is formed a surface film, which renders difficult the autohesion of the layers. Thus the elimination of the undesirable influence of oxygen processes upon the bond strength is possible by means of substances which are more active towards the radicals of the rubber than molecular oxygen is, or actively retard the processes of structurization. Our investigations in this direction are being continued.

From experiments in "freshening up" the surface of stored specimens it was apparent that during the interaction of the surface layer of the vulcanized rubber with oxygen there is formed an insoluble film of a crosslinked polymer. As these experiments showed, washing the surface of the specimens with naphtha does not lead to a return of the bond strength which is characteristic of the material when fresh specimens are plied up.

TABLE 3

ABSOLUTE (SEE NOTE) VISCOSITY OF BREAKER RUBBERS BASED ON
BUTADIENE (SKB) AND BUTADIENE–STYRENE (SKS-30),
DETERMINED BY THE METHOD OF EXTRUSION
THROUGH A DIE (CAPILLARY) AT 70°

Stock	Karrer plasticity	Viscosity η, in poises
SKB	0.48–0.55	$0.20 \cdot 10^6$
Natural rubber	0.45–0.55	$0.11 \cdot 10^6$
SKS-30	0.5–0.6	$0.75 \cdot 10^6$

Mechanical action upon the surface, capable of destroying the surface film and of freeing new layers of the stock which are not oxidized and not structurized, has an advantageous effect upon the bond strength. From this point of view we can understand the advisability of buffing before building up articles. Buffing uncovers fresh layers of the material, increases the area of contact between the layers and, finally, creates the conditions for the flow of material from one layer into another. All this has a favorable effect upon bond strength. Freshening up the surface with liquid bonding agent, as used in technological practice, enhances the tackiness of the surface and consequently improves building. In addition, it eliminates mechanical contamination, leads to partial mechanical destruction of the surface film, and causes swelling of the stock before building. All this ensures an improvement in the bond strength.

CONDITIONS OF AUTOHESION (= 'SAMOSLIPANIE')(FUSION
= 'SLIVANIE') OF BOUNDARY LAYERS. INFLUENCE
OF VISCOSITY, TEMPERATURE, PRESSURE AND
TIME OF CONTACT

The autohesion of pliedup layers is regarded as a diffusion process, effected by the movement of separate segments of the molecular chains of the rubber. From this point of view a number of papers[1] have studied the influence of the molecular weight, the flexibility of the molecular chains, the nature of the diffusion groups and so on upon the process of autohesion. Nevertheless it is not difficult to show that the diffusion movement of the separate segments is not sufficient for complete fusion of the pliedup layers. In particular, it is a known fact that layers of a soft vulcanizate do not cohere with each other, al-

though the mobility of the segments of the molecular chains is the same as for the raw rubber[2].

One essential condition for autohesion, obviously, is the existence of true flow in the material.   H. Mark considers that the viscosity of cemented materials should be not greater than 10^6 with a relaxation time of from 10^{-4} to 10^{-7} sec. The existence of true flow is particularly important for the joining of raw rubbers of different kinds, the thermodynamic characteristics of which do not promote a spontaneous diffusion process of autohesion.

TABLE 4

FLOWABILITY OF SKS-30 VULCANIZATION STOCKS AND RESISTANCE TO DYNAMIC PLY SEPARATION OF SPECIMENS PLIEDUP IN THE ORDER TREAD–BREAKER–TREAD, AS A FUNCTION OF THE AMOUNT OF VASELINE OIL IN THE BREAKER RUBBER

| | | | Dynamic ply separation | | |
| | | | Type of failure | | |
Addition of vaseline oil, parts by weight to 100 parts of raw rubber	Karrer plasticity	Flow-ability, 10^{-6} poises	Ply separation, %	Ply separation and partial failure, %	Average life, cycles
0	0.513	1.64	100	—	332
5	0.570	2.00	80	20	425
10	0.590	1.96	—	100	1160
20	0.670	3.23	—	100	1210

We carried out a large number of tests which confirmed the influence of the viscosity characteristics of the pliedup materials upon the strength of the bond between them.   Thus, in Table 3 we present data on the viscosity of vulcanization stocks prepared from raw rubbers of different viscosity.   Determination of the coefficient of viscosity arranges the raw rubbers in the following order: SBR > sodium-butadiene > natural rubber.   The pliedup rubbers came in the reverse order in respect of bond strength.

The addition of softeners, which increase the flowability of the stock, increases the bond strength within definite limits (Table 4).   Naturally, we must

TABLE 5

INFLUENCE OF PRESSURE USED DURING VULCANIZATION AT OPTIMUM CURE UPON THE RESISTANCE TO DYNAMIC PLY SEPARATION, THE ORDER OF PLYING UP BEING TREAD-BREAKER-TREAD

Pressure during vulcanization, kg/cm²	5	10	20	40	55
Average life, cycles	308	349	415	356	323
Nature of failure			Simple ply separation		

not overlook in this case the possibility of an adverse influence of the softener upon the strength of the material itself and of its blooming upon the surface of the pliedup layers.

The influence of pressure upon bond strength is shown in Table 5.   The effect of pressure is linked not only with the necessity for ensuring close contact between the pliedup layers, but also with the fact that where the pressure is sufficient there are set up tangential forces, causing forced flow of the material into unevennesses in the microrelief of the pliedup surfaces.

Finally the influence of the duration of contact (Table 6) does not call for

TABLE 6

RESISTANCE OF VULCANIZATES TO DYNAMIC PLY SEPARATION AS A FUNCTION
OF THE DURATION OF PRELIMINARY PLYINGUP PRESSURE OF
10 KG/CM² AT TEMPERATURE OF 40°

Duration of preliminary plying up pressure, hr		0	10	15
Average life,	1st series	323	582	1280
cycles	2nd series	316	—	840
Type of failure		Simple ply separation	Ply separation and partial destruction of breaker layer	

any explanation if we take into account the diffusion mechanism described above
and the influence of viscosity upon the process of fusion of the boundary layers.

INFLUENCE OF COMPOSITION OF VULCANIZATION SYSTEM
AND THE DYNAMICS OF VULCANIZATION

In connection with the influence of the flowability of pliedup stocks, considered above, upon their autohesion, the great importance of the dynamics of vulcanization upon bond strength becomes understandable.

In the process of vulcanization there takes place a gradual transition of the vulcanizing stock from the plastic flow state into the elastic as a result of crosslinking. As already indicated, the vulcanizate loses its capacity for cohesion after the formation of the spatial network. Thus the processes of fusion of the separate layers can occur only in the initial stage of vulcanization—as long as the stock is plastic and as long as no spatial network is formed.

Different vulcanization systems, differing in content and type of accelerator, have different kinetics and consequently require different times to reach the moment when flow no longer occurs. In general those systems which vulcanize more slowly promote more favorable conditions of autohesion of the pliedup layers and higher bond strength between the layers (Figure 3). On this question see also the paper by Dogadkin, Feldshtein and Pevzner[6].
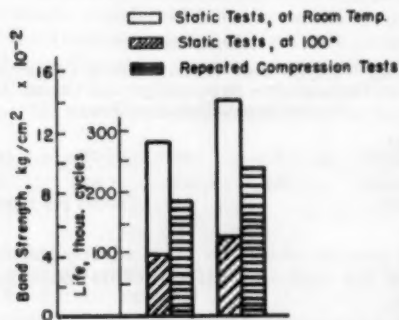
FIG. 3.—Bond strength between vulcanized rubbers as function of accelerator content in pliedup stocks.

Composition of vulcanization systems in parts by weight

	1	2
Sulfur	3.0	3.0
MBTS	0.8	0.5
DPG	0.8	0.5

From this point of view the most perfect vulcanizing systems are those which have an initial slowed-down (induction) period reaching optimum cure in a normal time. It is precisely this form of action of vulcanizing systems which is provided by the accelerator Sulfenamide BT. This may be seen from Figures 4 and 5, where we show the kinetics of change of flowability and of the
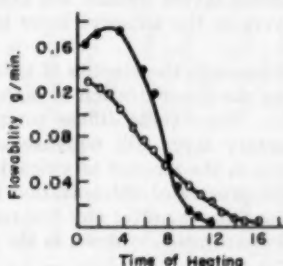
FIG. 4.—Change in flowability in the vulcanization of tread stocks with different accelerators. *1*, 0.5 part by weight of MBTS +1.0 part by weight of DPG; *2*, 1.0 part by weight of sulfenamide BT.

combination of sulfur in SBR stocks with this accelerator. For the same time for reaching optimum cure the stock with sulfenamide BT loses its flowability after 17 minutes while the stock with MBTS and DPG loses it after 12 min. It is quite evident that the conditions of autohesion where sulfenamide BT is used are more favorable, this being shown in the greater bond strength of the stocks, as may be seen from Figure 6.
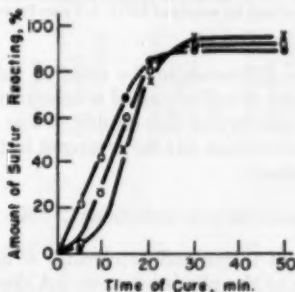
FIG. 5.—Kinetics of combination of sulfur during the vulcanization of tread stocks with different accelerators. *1*, 0.5 part by weight of MBTS +1.0 part by weight of DPG; *2*, 1 part by weight of Santocure; *3*, 1 part by weight of sulfenamide BT.

EFFECT OF COVULCANIZATION OF LAYERS AND THE INFLUENCE OF THE TYPE OF VULCANIZATION BONDS

The influence of the vulcanization groups is extremely important in another connection as well.

It is not hard to see that the maximum bond strength is attained only when the molecular chains of the raw rubber forming the boundary layer (after the occurrence to greater or less extent of the process of autohesion) are bound together by chemical crosslinks. An unvulcanized boundary layer does not promote bond strength. In other words, it is necessary to have covulcanization

of the pliedup layers, as being the formation of a single spatial network binding the molecules of both layers.

The process of covulcanization becomes evident to a greater degree if the rates of vulcanization are adjusted in the two pliedup layers so that the process takes place approximately with identical rate.   We must have in mind two cases : (1) the case where the pliedup layers contain the same polymer and (2) the case where the pliedup layers or the adhesive layer between them consist of different polymers.

In the first case, the difference in the kinetics of vulcanization of the pliedup layers will be determined by the concentration of ingredients of low molecular weight (sulfur, accelerator).   Since these diffuse comparatively rapidly, their concentration 'in the boundary layer will equalize as a result of diffusion. Thanks to this the difference in the amount of vulcanizing agents will not disturb the simultaneity of the process of vulcanization in the two layers.   The technologist in this case does not encounter any real restriction in the selection of the composition of the vulcanization systems in the pliedup layers.
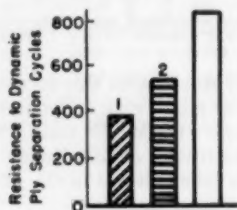
Fig. 6.—Resistance to dynamic ply separation of pliedup vulcanized rubbers with different accelerators. *1*, 0.5 part by weight of MBTS+1.0 part by weight of DPG; *2*, 1 part by weight by Santocure; *3*, 1 part by weight of sulfenamide BT.

In the second case the difference in the rates of vulcanization depends not only upon the concentration of sulfur and of accelerator, but also upon the concentration and different activity of the double bonds of the pliedup rubbers. Thus it is known that raw rubbers can be arranged in the following descending order of rate of vulcanization:

natural rubber>SKB (sodium-polybutadiene)>SKS (SBR)>butyl rubber.

In this case the diffusion of sulfur and accelerator is not capable of equalizing the rates of vulcanization of the pliedup layers.   A special selection of the vulcanizing systems is necessary in pliedup layers, to ensure simultaneity (synchronization) of vulcanization and at the same time to get the necessary bond strength between the layers.   It is nevertheless necessary to bear in mind that the solution of this problem is made more difficult as a result of the already noted diffusion equalization of the vulcanizing agents in the boundary layer.

In the case of different rubbers in pliedup stocks, not every vulcanization system is capable of ensuring covulcanization.   The absence of the proper effect of covulcanization is apparently the main cause of the adverse influence of an intermediate layer of natural rubber in the plyingup of SBR.   In fact the high bond strength of stocks in the raw state indicates the adequate compatibility and capacity for autohesion of natural and SBR rubbers.   In spite of this a film of natural rubber in the vulcanized states does not ensure the proper bond strength (although the film itself is sufficiently strong).

TABLE 7

INFLUENCE OF PARAQUINONE DIOXIME UPON BOND STRENGTH OF SKS-30 VULCANIZED RUBBERS, PLIED UP BY A NATURAL RUBBER BONDING AGENT AND CURED 75 MINUTES AT 143°

Rating No.	Composition of vulcanizing group, parts by weight to 100 parts by weight of raw rubber	Conditions of plying-up	Static ply separation in kg/cm and type of failure		Dynamic shear ply separation and type of failure	Relative service life t (with bonding agent) : to (without)
			At 25°	At 100°	Service life, t, sec.	
I	MBTS 0.3 sulfenamide BT 1.2 Sulfur 3.0	Without bonding agent	23.0; mixed	8.1; mixed	60; mixed	1.00
		With bonding agent	7.5; at the joint	1.5; at the joint	15; at the joint	0.25
II	Paraquinone dioxime 1.5 Sulfur 0	Without bonding agent	21.9; in the rubber	11.7; in the rubber	140; in the rubber	1.00
		With bonding agent	21.0; in the rubber	5.5; at the joint	40; at the joint	0.29
III	Paraquinone dioxime 1.5 Sulfur 0.5	Without bonding agent	19.0; in the rubber	11.5; in the rubber	100; in the rubber	1.00
		With bonding agent	20.0; in the rubber	6.0; in the joint	55; in the joint	0.55
IV	Paraquinone dioxime 1.5 Sulfur 1.0	Without bonding agent	18.5; in the rubber	10.0; in the rubber	100; in the rubber	1.00
		With bonding agent	18.0; in the rubber	7.7; in the joint	70; in the joint	0.70
V	Paraquinone dioxime 1.5 Sulfur 3.0	Without bonding agent	18.0; in the rubber	12.0; in the rubber	93; in the rubber	1.00
		With bonding agent	18.0; in the rubber	9.0; in the rubber	70; in the rubber	0.75

If a specimen of two pliedup strips of SKS-30 tread and breaker rubbers, cemented with a bonding agent of natural rubber, is placed in benzene after vulcanization, then simple swelling is capable of destroying the bond at the natural rubber-butadiene-styrene rubber boundary. This shows the absence of a continuous network at the boundary of the SBR and natural rubbers, i.e. the absence of the covulcanization effect.

A different state of affairs is observed if we incorporate pquinone dioxime as a vulcanizing agent in SKS-30. As may be seen from Table 7, in this case high bond strength is ensured even when using interlayers of natural rubber.

We can explain from the same angle the favorable influence of polychlorocompounds, in particular that of hexachloroethane, upon bond strength. Being an independent vulcanizing (or polymerizing) agent, hexachloroethane effects a significant enhancement of the service life of pliedup specimens of SBR (Table 8). The favorable influence of hexachloroethane was confirmed by

TABLE 8

DATA ON STATIC AND DYNAMIC PLY SEPARATION OF PLIEDUP SKS-30A
VULCANIZED RUBBERS CONTAINING HEXACHLOROETHANE

Composition of vulcanizing system	Static ply separation, kg/cm						Dynamic ply separation Tread-breaker	
	Tread-tread		Breaker-breaker		Tread-breaker		Average life, thous. cycles	Average temperature, ° C
	20°	100°	20°	100°	20°	100°		
DPG MBTS Sulfur	22.0	8.8	10.8	2.64	15-20	3.5- 6	210.0	94.5
DPG MBTS Sulfur + hexachloroethane	25.3	14.7	13.3	5.60	15-20	5.0-10	948.5	103.0
DPG MBTS Sulfur + zinc salt of trichloroacetic acid	Does not separate	14.3	18.0	6.10	16-20	5.5-10	1035.0	100.2

bench testing of tire casings (containing hexachloroethane in the formula of the breaker and tread rubbers); thus the average mileage of casings containing hexachloroethane was 3788 km (as against 2122 km for the reference casings).

Nevertheless, as our investigations showed, this favorable effect is connected also with the fact that polychlorocompounds which are antifatigue agents retard undesirable structural changes in the vulcanizate connected with thermomechanical degradation of the network.

INFLUENCE OF FILLERS

It has been established by work in the Chemical Technology department of the NIIShP (Tire Research Institute), and also by our experiments, that the presence of channel black, in comparison with other types of carbon black, noticeably enhances bond strength. This favorable influence of active carbon black, along with an undesirable reduction in the flowability of the stocks, may be explained, working from the following points: (1) channel black retards the process of vulcanization, (2) channel black forms chain structues of high thermal and mechanical stability, and (3) channel black interacts with free

polymer radicals formed during the mastication and mixing of the raw rubber, which leads to the setting up of a crosslinked rubber carbon black gel.

The two last-named phenomena lead to a strengthening of the material of the pliedup vulcanized rubbers directly in the contact zone.

PECULIARITIES OF THE MECHANICAL PATTERN AND OF THE FATIGUE OF THE BOUNDARY LAYER

Only in the limiting case of autohesion of stocks of the same composition after plying up and vulcanization is the surface layer not maintained, with the system becoming "monolithic" and being characterized by the bulk properties of the substance. In all other cases the system is not of one composition—in the boundary layer we will observe sudden alterations in one or other properties of the vulcanized rubber. This state of the boundary layer determines its particular behavior during deformation.

Mechanical nonuniformity and sharp alteration in the modulus and in the other properties of the vulcanized rubber lead to the setting up of zones of over-stressing under conditions of repeated deformation in the boundary layer, and these lead in turn to intensive processes of fatigue and destruction. These phenomena are being studied in greater detail in our physical laboratory (see the paper by G. L. Slonimskiĭ in the present symposium).

It must be added that in many cases there are in the boundary layer higher concentrations of oxygen and oxygen-containing compounds, as a result of the already mentioned phenomenon of absorption of air on the surface of the pliedup vulcanized rubbers. In particular this is noticeable at the cord-rubber boundary, since cord or loose structure undoubtedly contains a large amount of occluded and mechanically entrapped air. On account of this the chemical processes of fatigue take place more intensively in the surface layer than in the bulk of the rubber, which is one of the reasons for ply separation. In this connection it is necessary to develop means which are more effective than those used at present for combatting oxidation and fatigue in vulcanized rubber.

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FACTORS AFFECTING BOND STRENGTH BETWEEN THE ELEMENTS OF TIRES

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Ply separation in tires is one of the significant factors reducing their mileage. Under severe conditions this form of failure is often the main reason for discarding. This may be caused either by inadequate cohesive strength in the compounds and poor endurance under repeated deformation, or by poor adhesive properties in the pliedup vulcanizates, and also by poor adhesion between rubber and cord.

The nature of the failure of the tire body depends upon the cause of the separation. If this is due to unsatisfactory *cohesive* properties in the vulcanizates, the failure takes place in the body of the rubber itself with subsequent separation of the parts, without a clearly marked boundary. If the cause is insufficient *adhesion* of the vulcanized compounds or of the cord, we naturally observe a clear boundary between these materials.

Separation between the parts of a tire is dependent upon alternating tangential shear stresses, set up in the body during the rolling of the tire and attaining their maximum values in the breaker zone. The hysteresis losses in the tire, which are accompanied by heating of the tire, cause failure of the carcasses and in particular reduce their resistance to ply separation.

The adverse influence of heat buildup in the tire upon the physical properties of the materials and upon the bond strength between the parts of the tire is well known and need not be further discussed. Tires with synthetic rubber are marked by increased hysteresis. They are used at temperatures higher than for tires of natural rubber (Table 1).

Separation is one of the characteristic defects of synthetic tires, stripping of the tread being the predominant form of failure. It is therefore natural that prevention of the phenomena of stripping should be one of the main technical problems throughout the period of introduction of synthetic rubber in tire production. In spite of some successes, the problem is still not fully solved and the investigation of ways of enhancing bond strength between parts of the tire is one of the main tasks in further improvement of the service properties of tires.

MAIN FORMS OF FAILURE OF CONTEMPORARY TIRES OF SYNTHETIC RUBBER

As already indicated, the predominant form of failure of the early tires of synthetic rubber was stripping of the tread. The mileage of the tires was very

TABLE 1

HYSTERESIS LOSSES AND HEAT BUILDUP IN TIRES OF NATURAL AND SYNTHETIC RUBBER IN LABORATORY TESTS
(FORMULA TO SUIT THE PROPERTIES OF THE POLYMER)

Dimensions and model of tire	Polymer	Running on a smooth drum			Running on drum with cleats		Notes
		Hysteresis losses, kgm/rev.	Temperature in breaker zone °C	Temperature in carcass, °C	Temperature in breaker zone, °C	Temperature in carcass, °C	
260-20 (I-125)	Natural rubber	39	66	73	70	78	Drum with cleats 20 mm high; 40 km/hr
13V cord	Synthetic rubber	62	92	105	99	115	
7.5-20 (Ya-38)	Natural rubber	27	66	70	80	88	Drum with cleats 20 mm high; 50 km/hr
9T cord	Synthetic rubber	44	108	116	96	101	

low. Thus, 34 × 7 tires under actual service conditions on Class A roads failed through stripping of the tread after 5000 to 12,000 km running. Study of the defects revealed clear failure of the body of the breaker compound. Investigations were carried out in the NIIShP (Research Institute of the Tire Industry) directed toward enhancing the service properties of synthetic rubbers for tires.

In view of the increased hysteresis and lower endurance of synthetic rubber as compared with natural rubber, new requirements were formulated for the mechanical properties of synthetic rubber vulcanizates and a new scheme drawn up for specifications of tire bodies in which the modulus of the compounds increases progressively from the first layers of the carcass to the last, reaching the highest values in the breaker. Modulus is the stress for a given elongation. In the literature of rubber technology the designations M_{100}, M_{200} and so on are used to indicate the stresses at elongations 100%, 200%, and so on. The requirements for the physical properties of the tread compounds were also clarified in the same way.

The advantages of the proposed scheme of classification of compounds were repeatedly tested and confirmed by laboratory and service testing of synthetic rubber tires. There was a substantial increase in the endurance of the tires from the point of view of tread stripping and a sharp increase in the total mileage. Thus for instance in Table 2 we present the results of testing 34 × 7 tires, prepared to the previously used specifications and the new.

TABLE 2

ENDURANCE OF 34 × 7 TIRES OF 100% SYNTHETIC RUBBER AS A FUNCTION OF THE PHYSICAL PROPERTIES OF BREAKER AND CARCASS COMPOUNDS

Specification Parts of tire	Old All layers of carcass and breaker	New I			New II		
		First layers of carcass	Last layers of carcass	Breaker	First layers of carcass	Last layers of carcass	Breaker
Physical properties of the rubbers							
300% modulus, kg/sq cm	25	35	45	60	45	70	90
Heat buildup in repeated compression for given force amplitude, °C	110	92	103	85	103	77	75
Endurance in repeated shear, kc × 10⁻³	8	15	20	38	20	50	110
Laboratory testing							
Life to failure, km	300	2840			5500		
Temperature in breaker zone, °C	110	90			94		
Cause of failure	Stripping of tread	Stripping of tread			Tearing of carcass		
Road testing							
Class of roads	A B	A B			A B		
Total average life, km × 10⁻³	7 5	41 31			48 36		
Discard due to tread stripping, %	60 100	50 43			13 17		
Average life of discarded tires, km × 10⁻³	6 5	36 26			41 30		

TABLE 3

ENDURANCE OF 210-20 TIRES OF 100% SYNTHETIC RUBBER AS A FUNCTION OF THE
MODULUS OF THE COMPOUNDS AND OF THE DYNAMIC BOND
STRENGTH OF THE TREAD–BREAKER SYSTEM

Specification	Old	New I			New II		
Parts of tire	All layers of carcass and breaker	First layers of carcass	Last layers of carcass	Breaker	First layers of carcass	Last layers of carcass	Breaker
300% modulus of compounds kg/sq cm	25	40	60	75	60	70	100
Dynamic bond strength of tread-breaker system, ke	28	400			650		
Life of covers, km (in laboratory tests)	500	6000			10,100		
Temperature in breaker zone, ° C	90	91			95		
Main cause of failure	Stripping of tread	Stripping of tread and tearing of carcass			Tearing and ply separation of carcass		

Later the same conclusions were arrived at for tires of the new size 210-20 (recommended instead of 34 × 7), the construction of which was worked out with consideration of the peculiarities of synthetic rubber. (The method of indicating tire dimensions is unclear; *translator*). The results of laboratory tests of 210-20 tires, prepared to specifications with different schemes of arranging the compounds, are presented in Table 3.

Synthetic rubber tires in mass production were designed to use high-modulus compounds and with an appropriate distribution of these compounds in the carcass. In Tables 4 and 5 we present data characterizing the main types of failure of synthetic tires.

In laboratory tests, Table 4, the highest percentage of 210-20 tires failed through tread stripping and separation between the first and second layers of the breaker. In the case of 260-20, using rayon cords, ply separation in the carcass was also one of the main causes of failure. Under service conditions we clearly observe stripping of the tread, Table 5.

Here the relative number of tires discarded for this reason depends to a large extent upon the class of road. Whereas in service on Class A roads the number of 260-20 tires discarded as a result of tread stripping did not exceed 5%, on Class B roads it reached 22% and on Class C roads as much as 65%.

A detailed analysis of the type of failure of tires presently produced shows the predominance of the adhesion type of ply separation, without significant failure of the compounds. This is confirmed by experimental material obtained in our laboratory and in the Central Laboratory of the Yaroslavl Tire Works during study of the alteration in the physical properties of the compounds and in the bond strength between the main elements of the tire during the service of tires. For illustration we now present some data.

As is seen from Figure 1, the most important physical properties of tread and breaker compounds are maintained at a high level even after prolonged service of the tires (up to 60,000 to 70,000 km). On the other hand (Figure 2) the bond strength between the main elements of the tires is considerably reduced from the very beginning of the service of the tires.

It must be noted that in testing tire bodies discarded on account of ply separation after low mileage, we found the lowest bond strength figures in zones

TABLE 4

MAIN TYPES OF FAILURE OF 100% SYNTHETIC RUBBER TIRES IN LABORATORY TESTS

Size and model of tire	Where made	Number of tires tested	Average life to failure, km	Main defects on failure				
				Tread stripping	Separation between 1st and 2nd layers of breaker cord	Separation of carcass	Separation between carcass and breaker	Tearing of carcass
210-20 (1-124)	Experimental production	109	6000	26	32	8	6	27
210-20 (1-124)	Factory	28	3800	50	40	—	7	3
260-20 (1-125)	Experimental production	55	3300	34	13	49	—	3
260-20 (1-125)	Factory	29	2307	38	32	20	5	5

TABLE 5

MAIN TYPES OF FAILURE OF TIRES OF 100% SYNTHETIC RUBBER UNDER ACTUAL SERVICE CONDITIONS

Class of roads	Dimensions and model of tire	Where made	Average life of batch, km×10⁻³	Discard through natural wear of tread		Discard on account of production defects, %						
				%	Average life, km×10⁻³	Of total amount	Including					
							Tread stripping	Ply separation in carcass	Tearing of carcass	Tread wear	Other causes
A	260-20 (I-125)	Works	44	55	45	15	3	1	7	3	1
	260-20 (I-125)	Experimental production	42	38	52	19	5	1.5	9	0.5	3
	210-20 (I-124)	Experimental production	44	68	51	13	5	0.5	4	3	0.5
B	260-20 (I-125)	Works	35	43	45	18	9	1	5	2	1
	260-20 (I-125)	Experimental production	34	35	40	45	22	2.5	8	2.5	10
	210-20 (I-124)	Experimental production	34	50	45	38	20	0.5	7	6.5	4
C	260-20 (I-125)	Works	24	10	42	61	22	1	26	9	3
	260-20 (I-125)	Experimental production	20	17	37	67	44	4	6	1	12
	210-20 (I-124)	Experimental production	20	10	36	82	65	8	7	13	6
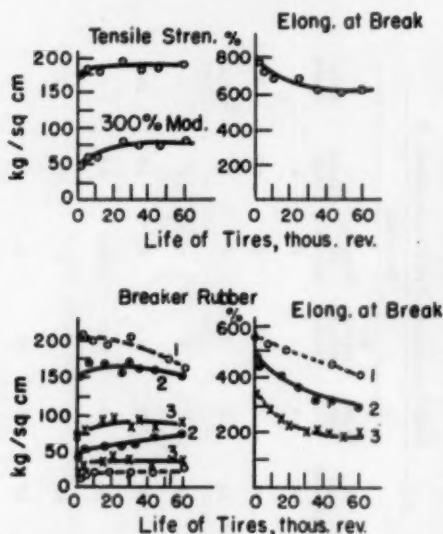
FIG. 1.—Alteration in physical properties of vulcanizates in service in tires.
1. 100% natural rubber; 2. 100% SKS-30A; 3. 100% SKB.

close to the stripping zone.   Thus the elimination of ply separation in synthetic
rubber tires should greatly influence the improvement of the service character-
istics of tires.

METHODS OF INVESTIGATION OF BOND STRENGTH IN
MULTI–PLY RUBBER AND RUBBER–CORD SYSTEMS

To investigate ways of enhancing bond strength between elements of tires,
we need methods of investigating this phenomenon in the laboratory which
will reproduce in model systems the type of failure which takes place during ply
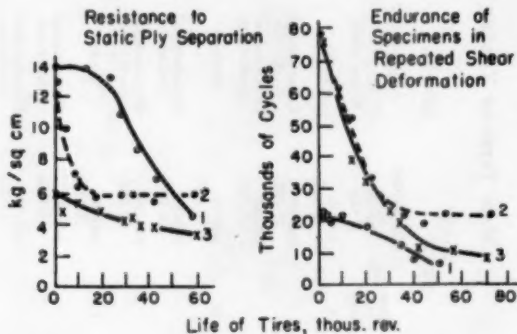
FIG. 2.—Bond strength of tread-breaker system in 260–20 tires as a function of mileage.
1. SKS-30A-SKS-30A; 2. SKS-30A-natural rubber; 3. SKS-30A-SKB.

TABLE 6

DYNAMIC BOND STRENGTH IN MODEL SYSTEMS AND ENDURANCE OF TIRES IN LABORATORY TESTS

No. of test	Type of polymer	Dynamic bond strength of the tread breaker system						Endurance of tires in laboratory tests					
		Repeated compression on 'Metallist' machine		Repeated compression on Goodrich flexometer		Repeated shear on breaker machine		200-20*		210-20*		200-20**	
		Number of cycles to failure	Relative endurance, %	Number of cycles to failure	Relative endurance, %	Number of cycles to failure	Relative endurance, %	Life to failure, km	Relative endurance, %	Life to failure, km	Relative endurance, %	Life to failure, km	Relative endurance, %
1	Natural rubber	393	100	130	100	11.7	100	8240	100	6373	100	8240	100
2	Tread of SKS-30A breaker of SKB	242	63	34	26	0.4	34	840	10	960	15	3363	100
3	SKS-30A	210	54	33	24	0.3	25	—	—	—	—	2380	73

* Testing at 40 km/hr on drum with cleats 20 mm high.
** Testing at 40 km/hr on drum with cleats 9.5 mm high.

separation of articles in service. None of the previous methods satisfies this
requirement. So far we have no methods at our disposal fully satisfactory
from this point of view. However various investigators have furnished
methods for determining the socalled dynamic bond strength in pliedup systems,
which made it possible, with an accuracy suitable for practical purposes, to
investigate the effect of various factors upon the bond strength.

In work in our laboratory we used mainly the following methods:

a) Dynamic separation of solid rubber specimens with a diagonal interlayer
in repeated compression on a 'Metallist' machine.

b) Dynamic separation of pliedup specimens with a normal interlayer in
repeated shear on M. A. Tsydzik's machine.

In addition, we used a number of other methods, in particular the method of
static separation of pliedup systems at elevated temperatures (from 20 to120°).

A preliminary check of the new methods of determining the dynamic bond
strength by comparing the results with those of laboratory tests of tires (as may
be seen, e.g., in Table 6) convinced us of the suitability of the new methods for
investigation of the phenomena of separation in pliedup systems. Moreover
this was confirmed in testing experimental tires under actual conditions of
service.

MAIN DIRECTIONS OF THE INVESTIGATIONS

The synthetic rubber tires adopted by the industry use butadiene styrene
rubber (SKS-30A) in the tread and sodium-butadiene (SKB) in the carcass and
breaker. The use of butadiene styrene rubber (SKS-30A) in all the main ele-
ments of tires has formed the subject of extensive experimental work, leading
to the output of large production batches. In the early period of adoption of
tires based on SKS-30A the occurrence of ply separation was a most pressing
and difficult problem. Investigation of the bond strength between the parts of
tires of SKS-30A, as may be seen from Table 7, revealed lower dynamic bond
strength of tread with breaker and lower temperature stability in static separa-
tion as compared with tires prepared with SKB breaker compounds. Therefore
in studying the phenomena of ply separation the main attention was paid to
pliedup systems based on butadiene/styrene rubber (SKS-3A).

From general theoretical considerations, and also from certain experimental
data, it might be supposed that one of the main causes of inadequate bond
strength in pliedup systems of butadiene/styrene rubber was the poor capacity
of stocks based on this rubber for true flow in the initial period of vulcanization
(in comparison with natural and sodium-butadiene rubbers). Thus in one
investigation by the NIIShP (Tire Research Institute) it was demonstrated
that in every instance the factors enhancing the flowability of pliedup stocks
also enhance the bond strength between them.

TABLE 7

BOND STRENGTH IN SPECIMENS FROM ACTUAL 9.00-20 TIRES

Type of polymer		Bond strength at ply separation in kg/cm at temperatures		Dynamic bond strength Cycles $\times 10^{-3}$
Tread	Breaker	18 to 20°	100°	
SKS-30A	SKB	5 to 7	1.4 to 2.0	139
SKS-30A	SKS-30A	6 to 11	1.4 to 3.0	86

The available experimental material showed that the separation of pliedup systems, in particular of butadiene/styrene rubber, is a considerably more complicated phenomenon and that the flowability of stocks is only one of many factors which may affect separation. Thus in the first stage of the investigations we decided to initiate experimental work in various directions and to study the effect of the following factors upon the dynamic bond strength.

a) The physical properties of the main tire compounds and combinations of them in multiply rubber and rubber-cord systems
b) The type of polymer
c) The principal compounding ingredients
d) The composition of the vulcanization ingredients and the conditions of vulcanization
e) The impregnating compositions for the cord
f) Certain factors in the technical process of tire manufacture.

Each direction represents an independent field of investigation, and in a review article it is not possible to deal adequately with the results obtained. We restrict ourselves below to certain experimental data relevant to dynamic bond strength in multiply vulcanized rubber systems, taking into consideration that there are individual reports dealing with the question of bond strength of rubber-cord systems.

DYNAMIC BOND STRENGTH IN SYSTEMS OF PLIEDUP COMPOUNDS AS A FUNCTION OF CERTAIN CHEMICAL–TECHNOLOGICAL FACTORS

Physical properties of the vulcanized compounds.—The dynamic bond strength in systems of pliedup compounds depends essentially upon the physical properties of the compounds (in particular upon the modulus) and upon the stress cycle in the specimen in repeated deformation. In stressing with a given amplitude of force, which from our point of view determines the conditions of operation of the rubber in the breaker zone, the dynamic bond strength increases markedly as the modulus of the rubbers increases, Table 8.

TABLE 8

DYNAMIC BOND STRENGTH IN SYSTEMS OF PLIEDUP COMPOUNDS AS A FUNCTION OF THE MODULUS AND OF THE CYCLE OF REPEATED DEFORMATION

Type of polymer		300% modulus, kg/sq cm		Cycle of repeated deformation of specimens		Dynamic bond strength cycles $\times 10^{-3}$	Temperature of specimen at instant of failure, °C
Tread	Breaker	Tread	Breaker	Deformation, %	Loading, kg/sq cm		
SKS-30A	SKB	52	38	40	20	360	116
SKS-30A	SKB	109	90	40	32	57	153
SKS-30A	SKB	109	90	23	20	2580	117

A series of experiments along these lines gave a basis for explaining the endurance of SKS-30A tires which resulted from further increasing the modulus of the compounds. The value of increasing the modulus in SKS-30A rubber is also affected by the comparatively high heat buildup in these rubbers in comparison with SKB rubbers. As separate investigations showed, the increased heat buildup in SKS-30A rubbers in repeated deformation is explained by the

different nature of the change in the elastic properties of SKS-30A vulcanizates (as compared with SKB vulcanizates), at a high temperature of testing.

Whereas for SKB the figures for the elastic properties increase sharply as the temperature is raised and, correspondingly, the internal friction losses decrease, for SKS-30A in many cases we even observe an increase in the internal friction losses as the temperature is raised, Figure 3. The heat build-up in SKS-30A tires is correspondingly higher than in those with SKB rubbers.

In Table 9 we present the results of laboratory tests of tires of SKS-30A manufactured with rubbers of differing modulus. On the basis of this experimental material, confirmed by the results of service tests of experimental tires, tire compound formulas based on SKS-30A, with higher modulus values, were proposed, ensuring higher dynamic bond strength as compared with the tires tested hitherto.

Type of polymer.—The test results shown in Table 10 show an essential difference in the dynamic bond strength in systems of pliedup compounds as a function of the type of polymer. For analogous deformation cycles the speci-
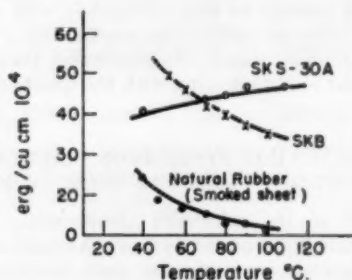
Fig. 3.—Mechanical losses of standard breaker compounds as a function of temperature.

mens of natural rubber are characterized by the highest dynamic bond strength. Specimens of SKS-30A, using vulcanizates with sharply increased modulus, do not fall short of the SKB specimens, while in comparison with specimens of pliedup SKS-30A and SKB compounds they show some superiority.

We must however keep in mind that in tire tests, System V (SKB breakers/SKS-30A tread) naturally has the advantage over System II, which is explained

TABLE 9

ENDURANCE OF 210-20 TIRES OF SKS-30A IN LABORATORY TESTS AS A FUNCTION OF THE MODULUS OF THE COMPOUNDS AND OF THE DYNAMIC BOND STRENGTH OF THE TREAD–BREAKER SYSTEM

Properties of compounds					Hysteresis and endurance of tires			
300% modulus, kg/sq cm			Dynamic bond strength of tread breaker system cycles $\times 10^{-4}$	Rolling losses, kgm/ rev.	Temperature, °C		Service life of tires, km	Main defects on failure of tires
Carcass	Breaker	Tread			Breaker	Tread		
21- 25	25	67	21	50.5	83	95	600	Stripping of tread
47- 61	95	67	312	45.5	83	92	5300	Stripping of tread and tearing of carcass
80-105	115	67	274	48.3	84	99	4700	Tearing of carcass
80-105	115	48	143	52.0	99	112	825	Stripping of tread
80-105	115	135	—	53.0	96	108	4200	Tearing of carcass

TABLE 10

DYNAMIC BOND STRENGTH OF TREAD BREAKER SYSTEM AS A
FUNCTION OF TYPE OF POLYMER

	Rubber	Type of polymer	Physical properties of rubber				Relative values of dynamic bond strength %	Temperature of specimens at instant of failure, °C
			300% modulus, kg/sq cm	Tensile strength, kg/sq cm	Shore hardness	Rebound elasticity, %		
I	Breaker	Natural rubber	65	301	55	60	100	123
	Tread	Natural rubber	123	338	68	38		
II	Breaker	Natural rubber	65	301	55	60	73	134
	Tread	SKB	59	105	60	30		
III	Breaker	SKB	67	91	59	38	55	131
	Tread	SKB	59	105	60	30		
IV	Breaker	SKS-30A	121	170	65	47	50	159
	Tread	SKS-30A	73	205	60	43		
V	Breaker	SKB	67	91	59	38	25	159
	Tread	SKS-30A	73	205	60	43		

by the higher elasticity of the SKS-30A tread compound. This factor has a
great influence upon the endurance of the tires, and apparently compensates
for the reduced dynamic bond strength in the boundary layer between the
breaker and tread.
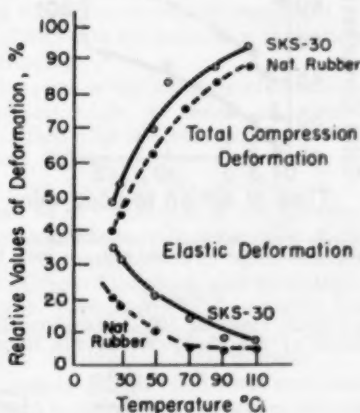
FIG. 4.—Plastic properties of natural rubber and SKS-30 as a function of
temperature (Goodrich Plastometer)

Along with the elevated elastic properties of vulcanizates of natural rubber,
the enhanced bond strength in this system, as already indicated, may be brought
about by the high flowability of the stocks in the initial period of vulcanization.
As shown in Figure 4, butadiene/styrene rubber and stocks based on it differ
from natural rubber and its stocks by the fact that in natural rubber the elastic
deformations practically disappear, while the plastic deformations reach their
maxima at lower temperatures: for natural rubber at 70 to 80°, and for SKS-30
at 110–130°.

The increase in the degree of thermo-oxidative destruction of butadiene/
styrene rubber, as well as the use of sodium-butadiene rubber with higher
initial plasticity, is furthered by the better spreadability of stocks at elevated

temperatures, Figure 5.   But, as was established in laboratory tests, Table 11, the use of synthetic compounds with high plasticity leads to a marked reduction in the endurance of the tires.   This must be explained by the fact that the physical properties and endurance of vulcanizates in repeated deformations is lowered as the initial plasticity of the synthetic rubber increases.

In comparative tests of SKS-30A from batches produced at different times attention was turned to their nonuniformity from the point of view of the dynamic bond strength of the pliedup systems.

A study of the causes of this nonuniformity led to the preliminary conclusion that the conditions of coagulation, insufficient removal of the emulsifier salts,
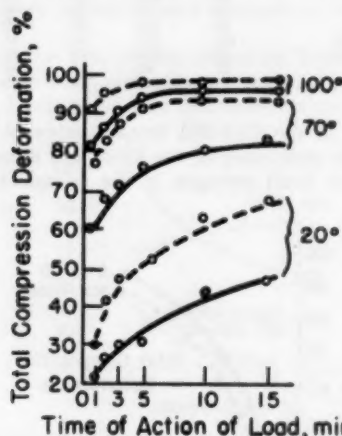
FIG. 5.—Plastic properties of SKS-30A stocks (Goodrich Plastometer).   Initial Karrer plasticity of SKS-30A: ——— initial 0.40; – – – initial 0.60.

TABLE 11

ENDURANCE OF 7.50-20 TIRES OF 100% SYNTHETIC RUBBERS AS A FUNCTION OF THE PLASTICITY OF THE RUBBER

Karrer plasticity of rubber	Type of polymer		Endurance of breaker rubber in repeated shear deformation cycles $\times 10^{-3}$	Dynamic bond strength of the tread-breaker system, cycles $\times 10^{-3}$	Service life of tires, km
	Tread	Breaker			
0.50	SKS-30A	SKB	569	190	12,050
0.60	SKS-30A	SKB	335	160	3,868

and certain other factors have a considerable influence upon the dynamic bond strength.

By a series of tests carried out in the laboratory during the investigation of SKS-30A specimens, coagulated with different electrolytes, we showed the significant influence of the coagulation agents, Table 13.

Changing the type of coagulation agents made it possible to more than double the bond strength in a system of pliedup compounds.

TABLE 12

DYNAMIC BOND STRENGTH OF TREAD–BREAKER SYSTEM AS A FUNCTION OF CERTAIN PROPERTIES OF SKS-30A

	Specimens of SKS-30A	
	I	II
Acetone extract, %	7.2	5.5
Ethanol-toluene extract, %	7.2	5.6
Physical properties of standard stock:		
300% modulus, kg/sq cm.	72	85
Tensile strength, kg/sq cm	260	270
Elongation at break, %	730	665
Permanent set, %	34	29
Dynamic bond strength of tread-breaker system, cycles $\times 10^{-3}$	305	480
Dynamic bond strength of breaker-cord system, cycles $\times 10^{-3}$	9	71
Relative endurance of tires, number of cycles to failure (in laboratory tests)	6	57

As may be seen from Table 14, experimental tires of synthetic rubber, made with a tread based on production SKS-30A or of SKS-30A, coagulated and washed under special conditions, showed different endurance under testing. Although the tests of these tires are not yet concluded, it is clearly evident that with the experimental SKS-30A the endurance of the tires is higher, particularly in regard to tread stripping.

Reclaim.—In order to show the influence of reclaim upon the dynamic bond strength of pliedup compounds, we tested, in combination with breaker of synthetic rubber, standard SKS-30A compounds, containing reclaim of various grades (R-20os, BR-23, BR-33 etc.).

As may be seen from Table 15, the introduction of reclaim, even in large amounts, did not lead to any reduction in the dynamic bond strength, which may be explained by two factors. On the one hand, the surface of the stocks containing the reclaim, is characterized by being much 'broken up' in comparison with the smooth surface of the stock with no reclaim; on the other hand the introduction of reclaim, particularly that prepared from tread rubber, gives rise to a high content of active carbon black in the stock, which has an advantageous effect upon the dynamic bond strength.

We added to the formula for SKS-30A tread compounds, reclaim in amounts up to 30 parts by weight to 100 parts by weight of the raw rubber. Tests in the laboratory, Table 16, and in service did not reveal any adverse effect upon bond strength between tread and breaker.

Carbon black and certain mineral fillers.—The influence of fillers upon the physical properties of synthetic rubber vulcanizates is well known. However we have not found any work in which there is a systematic study of the effect of these ingredients upon the dynamic bond strength in pliedup rubber systems.

TABLE 13

INFLUENCE OF COAGULATION AGENTS UPON DYNAMIC BOND STRENGTH BETWEEN SKS-30A COMPOUNDS

Type of coagulation agent	I	II	III	IV
Dynamic bond strength, cycles $\times 10^{-3}$	416	584	740	900
Relative change in bond strength, %	100	140	178	216

TABLE 14

Service Properties of 7.50-20 Tires of 100% Synthetic Rubber as a Function of the Properties of SKS-30A (Used in Tread)

Class of roads	Type of SKS-30A	Number of tires tested	Average road life per batch at given test level, km ×10⁻⁴	Continued in testing		Discard on account of production defects	Proportion of the above with tread stripping	
				%	Average road life, km ×10⁻⁴	Total, %	%	Average road life, %
A	Experimental	327	32	76	32	12	8	26
	Production	395	36	16	41	44	32	25
B	Experimental	575	29	51	32	30	22	26
	Production	413	33	5	28	45	28	23
C	Experimental	270	22	25	25	55	36	22
	Production	239	18	—	—	91	75	17

TABLE 15

DYNAMIC BOND STRENGTH OF TREAD (SKS-30A)-BREAKER SYSTEM
AS A FUNCTION OF RECLAIM CONTENT

Proportion of reduced parts by weight to 100 parts by weight of rubber	0	20	40	60	100
Content of fresh rubber, %	100	92.6	86.3	82.0	71.4
Dynamic bond strength, cycles					
R-20os reclaim	158	150	143	159	170
BR-23p reclaim	158	191	212	150	147
BR-33 reclaim	158	148	160	177	130

A comparison of fillers from this point of view shows the well known difficulties in connection with a significant change in the modulus, the elastic properties and other characteristics of vulcanizates as a function of the nature of the fillers and their content in the compound.

The main types of carbon black and certain mineral fillers were investigated by the authors in standard tread (SKS-30A) and breaker (SKB, SKS-30A) compounds over a wide range of equal volumetric proportions. The vulcanization recipe of the stocks was so adjusted that the modulus of the vulcanizates with one and the same volumetric amount of fillers varied within the narrowest possible limits. Thus, if for one and the same vulcanization recipe and 28 volumes of filler a tread stock has a 300% modulus within the limits 25 to 111 kg/sq cm, then after appropriate adjustment of the formulas the modulus lies within the limits 40 to 65 kg/sq cm. This made it possible to compare the values for dynamic bond strength for one and the same pattern of deformation of the specimens.

In Figure 6 we show the relative values of the fillers from the point of view of the dynamic bond strength of pliedup compounds. 100 units represents the value for specimens with channel black, which showed the highest endurance during testing.

Active anthracene black, particularly in systems entirely based on SKS-30A, falls short of channel black, having in this case no advantage over 'nozzle' black. 'Nozzle' black evidently is superior to furnace black, which is close to mineral reinforcing agent ('white black') from the point of view of dynamic ply separation bond strength. Mineral fillers such as zinc oxide and calcined magnesia fall short of carbon blacks.

Thus we have clear evidence of the different endurance of systems of pliedup synthetic compounds as a function of the nature of the filler.

TABLE 16

EFFECT OF INCREASING AMOUNTS OF RECLAIM IN TREAD
COMPOUNDS UPON THE BOND STRENGTH

No. of tread compound	Grade of reclaim	Content of reclaim parts by weight to 100 parts by weight of rubber	Dynamic bond strength, cycles $\times 10^{-3}$	
			Repeated compression	Repeated shear
1	—	—	289	1.6
2	R-20os	10	292	1.6
3	R-20os	20	246	1.9
4	BR-23p	30	225	1.7
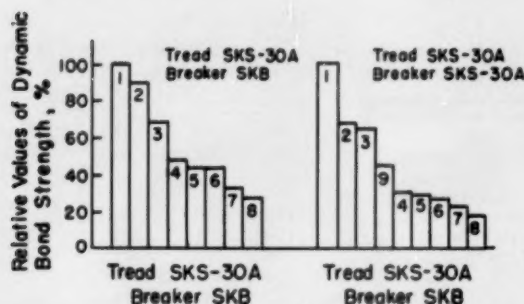
Fig. 6.—Dynamic bond strength of tread-breaker system as a function of the type of filler (equal volumetric filling, 17 parts by volume to 100 of rubber). 1—Gas black; 2—Anthracene black; 3—Nozzle black (oil-based furnace black); 4—Thermal black; 5—Furnace black; 6—'White black' (silica filler); 7—Zinc oxide; 8—Magnesium oxide; 9—Philblack A.

The superiority of channel black over anthracene may be connected with the fact that liquid hydrocarbons, adsorbed on particles of anthracene black, give rise to a weakening of the adhesion properties. In addition, the high 'dispersity' of channel black, its advantages from the point of view of reinforcing properties, and the higher resistance of stocks with channel black to oxidation. obviously have an advantageous influence upon the endurance of the specimens with this black to dynamic separation.

Plasticizers.—It is well known that tire stocks of synthetic rubber, in comparison with those of natural rubber, contain an increased amount of plasticizers. The addition of these materials and the selection of them have been governed up till now mainly by the necessity of improving the technological (working) properties of the stocks. Thus in a breaker stock of SKB there are up to 12 parts by weight of plasticizer to 100 of rubber; in breaker and tread stocks of SKS-30A, up to 10 phr of plasticizer.

Naturally, some 3 or 4 substances, chosen with reference to the specific action of each of them, are included in the plasticizers.

In standard tread and breaker stocks of synthetic rubber there are used mainly the following groups of plasticizers, Table 17.

The effect of plasticizers upon the dynamic bond strength in systems of pliedup compounds has up to now been studied very little and not systematically. At the same time, bearing in mind the active effect of plasticizers upon the plastic properties of raw rubber and stocks, upon the surface condition of the

TABLE 17

AMOUNT OF PLASTICIZERS IN SYNTHETIC RUBBER STOCKS

	Amount of plasticizer in various stocks, parts by weight		
Plasticizer	Tread SKS-30A	Breaker SKS-30A	Breaker SKB
Rubrax	—	3	5
Mazout plasticizer	7	—	—
Polydienes	—	5	5
Colophony	2	1	—
Paraffin wax	1	—	—
Fatty acids from vegetable oils	1–2	1	2

stock after calendering, and upon the physical properties of the vulcanizates, we may expect that plasticizers of different chemical classes will exhibit different effects upon the dynamic bond strength of the pliedup compounds.

In Table 18 we present some experimental data showing the effect of plasticizers upon bond strength in pliedup systems; SKS-30A tread-SKB breaker and SKS-30A tread—SKS-30A breaker.

As a basis we took standard mixes, containing different combinations of plasticizers. (Translator's note: 'Gudron'—'tar oil' or 'petroleum asphalt'. 'Rubber oil' is defined later as the product of dry distillation of 'amortized' (? scrap) rubber) the compositions of which are indicated above.)

In the tests we added to each of the basic stocks only one softener, in an amount corresponding to the combination adopted earlier. Simultaneously

TABLE 18

EFFECT OF PLASTICIZERS UPON DYNAMIC BOND STRENGTH
OF TREAD BREAKER SYSTEM

Before storage			After 3 days storage		
Plasticizer	Dynamic bond strength		Plasticizer	Dynamic bond strength	
	Cycles	%		Cycles	%
I. SKS-30A tread—SKB breaker					
Dibutyl phthalate	250	158	Rubber oil (light)	133	123
Rubber oil (light)	208	132	Rubresin B	133	123
Rubber oil (heavy)	200	126	Yarresin B	117	108
Polydienes	183	116	Rubrax	108	100
Rubrax	166	105	Combination of plasticizers	108	100
Combination of plasticizers	158	100	Kapol'	108	100
Rubresin B	142	90	Petroleum-polymer resin	100	92
Yarresin B	125	79	'Gudron' plasticizer	92	85
Kapol'	125	79	Polydienes	92	85
Petroleum-polymer resin	125	79	Mazout plasticizer	75	70
Mazout plasticizer	116	70	Colophony	75	70
Colophony	92	58			
II. SKS-30A tread—SKS-30A breaker					
Rubresin B	633	234	Rubber oil (light)	325	140
Polydienes	562	210	Rubrax	287	123
Yarresin B	550	206	Polydienes	279	120
Rubber oil (light)	425	160	Rubresin B	266	114
Rubber oil (heavy)	400	150	Yarresin B	242	104
Rubrax	345	129	Combination of plasticizers	233	100
Dibutyl phthalate	268	101	Rubber oil (heavy)	225	96
Combination of plasticizers	267	100	Dibutyl phthalate	183	80
Mazout plasticizers	233	87	'Gudron'	142	61
Kapol'	133	50	Mazout plasticizer	116	50
Petroleum-polymer resin	117	43	Petroleum-polymer resin	100	46
			Colophony	75	32

we carried out some adjustment of the vulcanization recipe so that there would not be any essential difference in the values of the modulus of vulcanizates with different plasticizers.

Determinations of bond strength, and of a number of other properties of the stocks, were carried out immediately after calendering and after three days' storage of the blanks at room temperature followed by plyingup.

From Table 18 we clearly see the different effect of the plasticizers upon the dynamic bond strength of the systems under investigation. Both the absolute values of endurance of the specimens and the relative role of each plasticizer depend upon the type of polymer in the pliedup systems. On plyingup the specimens after preliminary storage of the blanks, the bond strength naturally is considerably lower in comparison with specimens prepared immediately after calendering.

In systems based entirely on SKS-30A the highest bond strengths are observed for specimens with alkyl-phenol resins. (Rubresin B, Yarrezin B), rubber oil, polydienes and Rubrax. On the other hand, mazout of paraffin-base petroleum, 'gudron', petroleum-polymer resin, Kapol' etc., in the amounts investigated, significantly reduce the endurance of the specimens in comparison with the accepted combinations of plasticizers.

In SKS-30A tread—SKB breaker systems the addition of dibutyl phthalate and of rubber oil had an advantageous effect upon bond strength. Polydienes, while having an advantage in the case of specimens prepared without preliminary storage, caused a noticeable reduction in bond strength in tests on specimens with preliminary storage. Specimens with alkylphenol resins, while showing no advantage in a first series of tests, proved to have higher endurance in a second series of tests (with preliminary storage of the blanks).

TABLE 19

DYNAMIC BOND STRENGTH IN SYSTEMS OF PLIEDUP COMPOUNDS
AS A FUNCTION OF FATTY ACID CONTENT

Amount of fatty acid				
Parts by weight without counting fatty acid in the synthetic rubber	Parts by weight, counting fatty acid in the synthetic rubber		Dynamic bond strength, cycles	Relative change in bond strength, %
I. SKS-30A tread—SKB breaker				
0	0.9	0.5	117	100
0.5	1.4	1.0	166	142
1.0	1.9	1.5	125	107
3.0	3.9	3.5	108	92
5.0	5.9	5.5	100	85
II. SKS-30A tread—SKS-30A breaker				
0	0.9		350	100
0.5	1.4		242	70
1.0	1.9		183	52
2.0	2.9		166	48
5.0	5.9		100	28

Colophony, mazout, 'gudron' and petroleum-polymer resin, just as in systems wholly of SKS-30A, showed an adverse effect upon the dynamic bond strength.

Work on the investigation of plasticizers is being continued and will in the future make it possible to judge the probable chemical mechanism of different chemical groups. However on comparing the dynamic endurance of the specimens with the other properties of the stocks and of vulcanizates it is first of all apparent that certain substances which have an advantageous influence upon the tackiness of the stocks are even more effective from the point of view of bond strength. Thus, for stocks based on SKS-30A, containing the usual combination of plasticizers, the tackiness, determined on the Behre apparatus, was about 1900 g/cm as against 2500 to 3000 g/cm for the stocks with alkyl-phenol resins, polydienes or rubber oil. However this rule was not confirmed in all cases.

Bearing in mind the specific effect of fatty acids (from vegetable oils) upon the properties of raw rubber and of stocks, in comparison with other plasticizers, we studied their action in the same systems of pliedup compounds, Table 19.

As a reference standard we took specimens prepared from stocks containing no fatty acids.

The addition of fatty acids to SKS-30A stocks has an adverse influence upon the dynamic bond strength with as little as 0.5 parts by weight of fatty acid to 100 parts by weight of raw rubber. In SKS-30A—SKB pliedup rubber systems fatty acids in amounts of 3 parts by weight and above also reduce the bond strength.

This adverse influence of fatty acids may be a result of their capacity for migration, and also of their activating effect upon destructive processes in the raw compounds.

Thus, a proper choice of the group of plasticizers is an important factor from the point of view of separation in systems of pliedup compounds.

Vulcanization system.—We shall not dwell in detail upon the very important question of the effect of the vulcanization recipe and of the conditions of covulcanization of pliedup compounds upon the bond strength, as this will be dealt with in other papers.
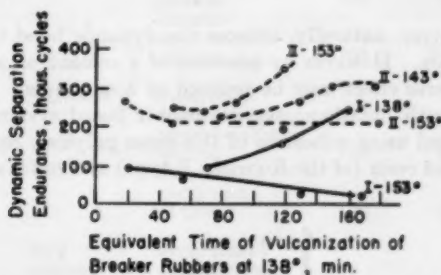
Fig. 7.—Dynamic bond strength as a function of temperature and time of vulcanization of SKS-30 breaker SKS-30 tread system. I—vulcanization system: BT Sulfenamide+MBTS. II—vulcanization system: MBTS+DPG.

In developing standard tire stocks based on synthetic rubbers, we investigated in detail the effect of different vulcanization accelerators, of their proportion relative to the sulfur, and also of the vulcanization temperatures.

For systems based on butadiene/styrene rubber there is repeated confirmation of the superiority of sulfenamide BT over other accelerators.

The results shown in Figure 7 indicate that the dynamic bond strength increases with equivalent time of vulcanization at temperatures 133 to 143°. Increasing the temperature to 153° led to a certain reduction in the endurance of the specimens and also of tires made entirely of SKS-30A. These results, which still call for further study, are evidence of the necessity for studying the optimum conditions of vulcanization for synthetic rubber tires from the point of view of their endurance in dynamic operation.

Some factors in the technology of tire production.—The significant effect of certain technological factors upon dynamic bond strength in pliedup rubber systems and upon the endurance of synthetic rubber tires in respect of separation has been established experimentally. The extent of the influence of this or the other factor is to a large extent governed by the materials used. The type of polymer, the composition of the stocks, the type of cord and other factors must all be carefully considered.

TABLE 20

DYNAMIC BOND STRENGTH IN SYSTEMS OF PLIEDUP SKS-30A
COMPOUNDS AS A FUNCTION OF THE CEMENT LAYER

	Type of cement	Tackiness (Behre), g/cm	Relative endurance to dynamic separation, %		Endurance of 260-20 tires in laboratory tests, km
			Repeated compression	Repeated shear	
	Without cement layer	1100	100	100	—
1	Smoked sheet, channel black	2520	14	20	100
2	SKS-30A, channel black, colophony	1950	36	74	800
3	SKS-30A, channel black Rubresin B	2380	82	94	2123

The cement layer, naturally, reduces the dynamic bond strength between pliedup compounds. However by selection of a cement of appropriate composition this adverse effect may be reduced to a minimum. As may be seen from Table 20, with butadiene/styrene rubber based systems advantageous results are obtained using adhesives of this same polymer, containing channel black, alkyl-phenol resin (of the Rubresin B type) and sulfenamide BT.
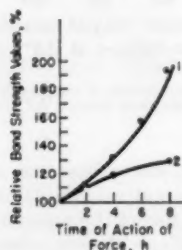
FIG. 8.—Dynamic bond strength of tread-breaker system as a function of molding pressure.
1. SKS-30A—SKS-30A; 2. SKS-30A—SKB.

Treating the lower surface of the tread with No. 3 cement brought about a significant enhancement in the endurance of SKS-30A tires in laboratory testing, and also in testing under service conditions. Premolding prior to vulcanization whether of pliedup specimens or of tires (keeping on the expanded airbag), naturally has an advantageous effect upon enhancement of bond strength, Figure 8 and Table 21.

Prolonged storage of blanks and parts of tread and breaker compounds has an adverse effect upon the values for bond strength between them in the vulcanized state. The most pronounced reduction in bond strength takes place when the blanks are stored at high temperature, Figure 9.

TABLE 21

ENDURANCE OF 260-20 (13V) TIRES AS A FUNCTION OF CERTAIN
TECHNOLOGICAL FACTORS IN LABORATORY TESTING

Type of polymer			Conditions of manufacture		
Tread	Breaker		Without prior storage of parts	Prior storage of parts for 24 hrs	Premolding on air-bag, 3 hrs
SKS-30A	Natural rubber	Separation resistance in tread-breaker system	100	105	82
		Relative endurance of tires	100	103	98
SKS-30A	SKB	Separation resistance in tread-breaker system	100	110	143
		Relative endurance of tires	100	280	210
SKS-30A	SKS-30A	Separation resistance in tread-breaker system	100	55	127
		Relative endurance of tires	100	65	120
New polymer	New polymer	Separation resistance in tread-breaker system	100	21	70
		Relative endurance of tires	100	32	62

Note: The separation resistance was determined at 70° for specimens from complete tires.

It is established that in the case of butadiene/styrene rubber (SKS-30A) careful roughening of the surface of the parts after storage leads to a significant recovery of dynamic bond strength, which is evidence of considerable changes in the surface layers of the parts in the course of storage, Table 22.
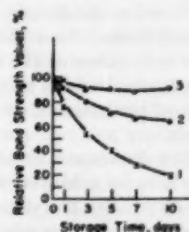
FIG. 9.—Dynamic bond strength of tread-breaker system as a function of duration of storage of parts. Curve—1—SKS-30A—SKS-30A; 2—SKS-30A—SKB; 3—SKB-SKB.

TABLE 22

EFFECT OF TIME OF STORAGE AND OF TREATMENT OF THE SURFACE OF THE
TREAD UPON THE DYNAMIC BOND STRENGTH OF A
SKS-30A—SKS-30A SYSTEM

Conditions of preparation of specimens	Relative values of dynamic bond strength, %
Without preliminary treatment (storage 24 hrs)	100
Preliminary treatment with cement	70
Preliminary roughening and treatment with cement	90
Storage 10 days, preliminary treatment with cement	50
Storage 10 days, preliminary roughening and treatment with cement	75

The above examples show the necessity of strict regulation of the technological process in preparing tires using synthetic rubber and prove that technological procedure must be carefully worked out with reference to its effect upon the endurance of the finished articles.

CONCLUSIONS

1. Ply separation of tires is one of the essential factors reducing their mileage, particularly under difficult service conditions. Enhancement of the dynamic bond strength between elements of the tires is a most important line of study for increasing the mileage of tires based on synthetic rubber.

2. An analysis of defects in tires failing as a result of separation shows that for a given level of technical proficiency in handling synthetic rubber the adhesion type of separation between pliedup compounds or between rubber and cord (of viscose filament) is predominant. This form of failure is particularly characteristic of tires with vulcanizates based on butadiene/styrene rubber in all the main parts.

3. In investigations concerning separation phenomena in tires, decisive importance attaches to methods of determination of bond strength under conditions of dynamic loading of pliedup vulcanizates and rubber cord systems.

We still do not have methods which could be regarded as fully satisfying the requirements proposed. However a series of methods have been provided which make it possible to assess, with an accuracy suitable for practical purposes, the effect of this or that factor upon the bond strength and to show the advantages and inadequacies of pliedup systems from the point of view of the operation of tires under actual service conditions.

4. The experimental results obtained show that the dynamic bond strength in pliedup systems, as also the endurance of the tires in relation to separation resistance, is determined by a complex body of physico-chemical and technological factors, by the construction of the articles, and also by the pattern of loading under repeated deformations.

The general theoretical ideas developed in articles by some investigators, that the highest bond strength is to be achieved where full adhesion of the raw pliedup stocks takes place, as shown by the disappearance of boundaries between them, and that in all cases the factors which enhance the flowability of the stock enhance also the bond strength between them, were not confirmed experimentally.

Further detailed investigation is required to explain the mechanism of separation of pliedup systems under conditions of repeated deformation.

5. An experimental demonstration has been given of the effect of a series of factors upon the dynamic bond strength in systems of pliedup vulcanizates and upon the endurance of tires based on synthetic rubber.

a) The physical properties of the vulcanized compounds and the way in which they are distributed in the tire according to their modulus have a considerable effect. The well known increase in the modulus of compounds in the breaker and carcass of synthetic tires has a favorable influence upon the endurance of the tires from the point of view of the bond strength between their parts.

b) Systems of pliedup vulcanizates based on synthetic rubbers (SKB, SKS-30 and SKS-30A) fall short of those based on natural rubber (smoked sheet), this being explained by the increased elastic deformations of the synthetic stocks in comparison with natural, and also by the better elastic and fatigue properties of the vulcanizates based on natural rubber.

c) Increasing the amount of thermo-oxidative degradation of butadiene/styrene rubber, as also the initial plasticity of sodium-butadiene rubber leads to a reduction in the elastic deformation of the stocks and to better flow in the initial period of vulcanization. However the dynamic bond strength in pliedup rubber systems decreases sharply as the plasticity of the synthetic rubber is increased, which is explained by the deterioration in the physical and fatigue properties of the vulcanizates based on rubbers with high plasticity.

d) The presence in production butadiene/styrene (SKS-30A) rubber of unremoved salts of Nekal, and the increased content of fatty acids lead to a significant reduction in the dynamic bond strength in standard constructions and to a sharp reduction in the endurance of the tires in actual service conditions. Altering the type of coagulation agent led to a more than two fold increase in the dynamic bond strength.

The mechanism of the action of the coagulation agents and the requirements placed on the rubber from this point of view form the subject of further investigations.

e) The addition of reclaim to tread rubbers based on SKS-30A in 10 to 20 phr has no adverse effect upon the dynamic bond strength values in standard systems or in the finished articles.

f) The type of filler and its amount in the compounds affect the dynamic bond strength. From this point of view channel black has a clear superiority over other types of black, and in particular over active anthracene black.

g) A difference in dynamic bond strength has been established in systems of pliedup vulcanizates containing plasticizers of different chemical classes; in particular, for systems based on butadiene/styrene rubbers we have established the superiority of such substances as alkyl-phenol resins (Rubresin B type), polydienes and rubber oil (product of dry distillation of 'amortised' rubber).

Fatty acids have a negative effect upon dynamic bond strength, particularly in systems based on butadiene/styrene rubber, which is presumably explained by their capacity for migration and their activation of degradation in the raw rubber. The permissible amount of fatty acids in Soviet tire compounds should not be more than 1 to 1.5 parts phr.

h) For vulcanized compounds based on butadiene/styrene, we have confirmed the advantageous influence of the accelerator sulfenamide BT upon dynamic bond strength.

The significant effect of the type of vulcanization of standard systems and

articles upon bond strength and upon the endurance of SKS-30A tires is demonstrated.

i) It is established that certain factors in the technological process of tire manufacture affect the bond strength and the endurance of synthetic rubber tires.

The cement interlayer, naturally, reduces the bond strength. It is nevertheless possible to reduce this adverse effect to a minimum by choosing a cement of appropriate composition. Thus, for systems based on butadiene/styrene rubber we have established the superiority of cement interlayers of the same polymer, containing Rubresin B, channel black and sulfenamide BT.

Premolding of parts and complete tires before vulcanization has an advantageous effect upon bond strength.

Prolonged storage of parts before building, particularly at elevated temperatures, leads to a considerable reduction in the dynamic bond strength and endurance of the tires, particularly in the case of the use of SKS-30A compounds in all the principal parts.

6. Study and consideration of the factors affecting dynamic bond strength in pliedup tire systems and in rubber-cord systems have made it possible to develop the technology of manufacture of tires based entirely on butadiene/styrene rubber superior to previously tested tires in service properties.

7. In spite of a number of measures which effect an enhancement of the dynamic bond strength between parts of synthetic rubber tires, the phenomenon of ply separation in service is still not fully eliminated, and research in this field must be continued.

DETERMINATION OF STATIC AND DYNAMIC BOND STRENGTH BETWEEN VULCANIZATES *

M. M. REZNIKOWSKIĬ

Methods employed for the determination of bond strength between vulcanizates may be classified as static or dynamic. Each of these groups has its own advantages and shortcomings.

One undoubted advantage of the majority of static methods is that the tests are carried out under conditions where the stresses and deformations which determine ply separation may be measured directly. It is at the same time easy to determine the temperature since the specimens undergoing ply separation may be thermostatically conditioned.

Nevertheless the practical value of the results obtained in static tests is very limited. In the first place, the character of the stresses governing ply separation in no way reproduces the true picture of the service life of multiply vulcanized rubber articles (in particular, tires), and, secondly, the resistance to ply separation for a single loading, for a number of reasons, may not indicate the endurance of the articles under repeated deformation.

In dynamic tests we use the endurance under repeated deformations as a criterion of bond strength, presuming that the dynamic pattern of testing in some way reproduces the pattern of service of the material in the article.

Unfortunately, the index of service life of any test specimens depends, in a complex manner which we do not in general understand, not only upon the bond strength between the vulcanizates, but also upon the stresses, deformations and also temperatures developed in the boundary layer. These parameters (stress, deformation and temperature) depend in their turn upon the elastic and relaxation properties of the vulcanizates from which the test specimen is made up. If the testing of the specimens is carried out in a dynamic pattern essentially different from that of service, then the results may be quite contrary to the behavior of the materials in an article. The selection of a rational method of dynamic testing applicable to tire compounds is particularly complicated on account of inadequate knowledge of the dynamic pattern of the operation of the component parts of the tire.

Summarizing, we see that in investigations and tests of bond strength between vulcanizates we are obliged to use both static and dynamic methods. The static methods, allowing a quantitative interpretation of the results, must be considered more reliable for investigations in the fields of adhesion and covulcanization, particularly in cases where we are studying the effect of factors which essentially alter the properties (above all, the elastic and hysteresis properties) of pliedup vulcanizates.

In selecting a rational method of testing bond strength between vulcanizates for multiply articles operating under conditions of dynamic stressing, primary importance attaches to the reproduction by the test apparatus of the main

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peculiarities of the dynamic pattern of loading of the vulcanized rubber in the article.

Independently of the method adopted, a basic difficulty arises in the determination of bond strength connected with the fact that ply separation by no means always takes place at the boundary surface between the compounds. Where the ply separation takes place partly in one of the compounds, the value determined proves to depend not only upon the bond strength, but also upon the internal strength (the cohesion) of the pliedup compounds.

The improvement we have devised concerns the method of preparation of the specimens for testing, and is as follows: we apply to the surface of one of the pliedup sheets, by means of a special perforated stencil, a thin layer of talc in small circles of diameter 1.5 mm, arranged in a checkerboard pattern at a distance of 2 mm from each other. The application of the talc calls for a certain amount of skill and great accuracy. After application to the rubber, the perforated metal stencil must be pressed on it with considerable force so that the irregularities on the surface of the rubber, which inevitably occur on the calendered sheet while it is left standing, shall not prevent proper application of the talc. Then the talc is dusted (screened through silk) on the perforated stencil. After this the sheet, with the stencil pressed on it, is turned over and excess talc shaken off by tapping gently. After removal of the stencil a visual inspection is made to see whether the talc is applied properly.

Plyingup and vulcanization are carried out in the usual sequence.

Since the presence of the talc layer prevents adhesion, the effective surface of the joint between the rubbers is reduced. The extent of this reduction, determined by the method of applying the talc, may be regarded as a constant factor if this operation is strictly standardized. The reduction of the effective surface of the joint causes ply separation depending upon the ratio between the bond strength on the boundary and the cohesion of the pliedup compounds.

By using the above method of plyingup, it is possible to determine the bond strength of vulcanizates of different or of the same composition. A comparison of the indices of resistance to ply separation in the former and latter cases makes it possible to assess separately the part played by the forces of cohesion and autohesion in a given strength of bond between vulcanizates. Bearing in mind the ideas stated above, a trial of the proposed improvement was carried out by the widely-used static method of determination of the force of ply separation.

The reproducibility of the test results is demonstrated in Table I. Here we present data on 21 tests of bond strength in a SKS-30 tread—SKS-30 breaker system, carried out on specimens from different batches of the plasticized product, with different mixing charges and vulcanization basis. From the table it is seen that the scatter of the bond strength values does not exceed that usually observed in tests of this nature.

For laboratory assessment of resistance to ply separation under repeated deformation a number of methods have been proposed in recent times.

The following are worthy of note: the method of repeated compression of diagonally joined specimens, developed in the laboratory of the Yaroslavl Tire Works; the method of repeated compression of cubes of tread rubber with a diagonally running interlayer of breaker rubber, proposed by the chemical technology division of the NIIShP (Tire Research Institute); the method of repeated compression of cylindrical specimens of analogous structure on the Goodrich Flexometer[1], developed by the Moscow Lomonosov Institute of Fine Chemical Technology and the Moscow Tire Works[2]. V. L. Biderman proposed

TABLE I

REPRODUCIBILITY OF TEST RESULTS

x	$\bar{x}$	$x - \bar{x}$	$(x - \bar{x})^2$	$\dfrac{\sqrt{\Sigma(x-\bar{x})^2}}{n}$
11.9	10.84	1.06	1.12	1.27
12.0		1.16	1.35	
12.6		1.76	3.50	
12.0		1.16	1.35	
11.5		0.66	0.435	
10.1		−0.74	0.548	
10.4		−0.44	0.193	
11.5		0.66	0.435	
11.6		0.76	0.577	
10.9		0.06	0.0036	
11.2		0.36	0.129	
12.2		1.36	1.85	
12.5		1.66	2.76	
11.5		0.66	0.435	
10.9		0.06	0.0036	
8.9		−1.94	3.76	
9.1		−1.74	3.03	
8.4		−2.64	6.98	
9.6		−1.24	1.54	
9.5		−1.34	1.80	
9.3		−1.54	2.37	
227.6			34.169	

Note: x = ply separation force, kg/cm. $\bar{x}$ = mean ply separation force, kg/cm. $\dfrac{\sqrt{\Sigma(x-\bar{x})^2}}{n}$ = mean square deviation in ply separation.

carrying out ply separation tests by subjecting specimens to repeated shear deformation in which the plane of the joint of the pliedup compounds is arranged at right angles to the direction of shear. V. L. Biderman's proposal was taken as a basis for the method we developed, which we describe below.

Here we must indicate one basic difficulty connected with the quantitative assessment of resistance to ply separation in any laboratory method. The point is that in a number of cases, particularly during the testing of specimens pliedup without using a bonding agent, ply separation does not occur, and instead one of the compounds fails. Obviously the number of cycles to failure in this case is in no way indicative of the bond strength. The conclusion moreover that there is no ply separation, or in other words that the strength at the joint is close to the strength of the material, is also unfounded, since, not knowing accurately the stress distribution in the specimen under test we cannot be sure that the ply separation stress in the plane of the joint is not lower than that which caused failure elsewhere.

From the point of view of method the question of vulcanization of the pliedup specimens appears of essential importance. The point is that specimens pliedup in the usual way are vulcanized in molds and after performing the vulcanization is carried out under conditions of approximately constant volume. On the other hand in tire vulcanization there is a routine of constant pressure, applied by superheated water from the bag side.

In order to eliminate this difference we vulcanized the specimens in a plunger mold, Figure 1, giving vulcanization with constant pressure. As already stated, we selected as a basis the method of repeated shear deformation, in which the plane of the joint in the specimen under test was arranged per-

FIG. 1.—Diagram of plunger mold.

pendicular to the direction of shear, Figure 2. The test specimen was clamped
between the horizontal platens of a so-called shear machine and subjected to
testing at a frequency of 500 c/min.

In a series of special tests planned with a view to working out a method, we
studied the effect of the dimensions and shape of the specimen, of the amplitude
of oscillation of the moving platen and of the magnitude of the vertical com-
pression. We compared the data obtained with constant vertical deformation,
with the data obtained with constant compressive force.

As an outcome of the tests, it was shown that to obtain the most reliable
and reproducible results it is desirable to carry out the tests with constant verti-
cal deformation.

On studying the part played by the magnitude of the compression and the
amplitude of movement, we observed that in both cases the determining factor
was the amplitude of the shear undergone by the specimen. The data obtained
in the investigation of the dependence of the number of cycles to failure upon
the angle of shear are presented in Figure 3. The tangent of the angle of shear
is determined as A/H, where A is the amplitude of oscillations of the moving
platen and H the distance between the platens.

In Figure 3 we plot the data obtained in tests under conditions of constant
vertical deformation: in one series of tests we varied the amplitude of shear,
while in another series with constant amplitude of shear we varied the com-
pression. The data presented relate to the testing of a tread-breaker system
based on SKS-30, pliedup without using a bonding agent. A somewhat unex-
pected feature was the dependence observed between the angle of shear and the
nature of the failure of the specimen. It was found that increasing the ampli-
tude of shear in the range 50° to 60° leads not only to a sharp reduction in the
service life, but also to a qualitative alteration in the nature of the failure of the
specimens.
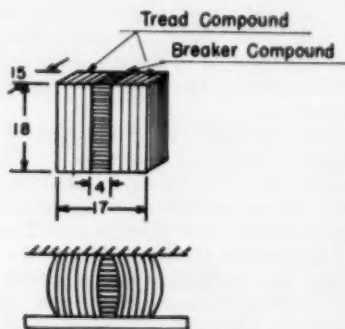
FIG. 2.—Construction of the specimen and scheme of loading in repeated shear testing.

The circumstance that with an angle of shear of 60° almost 100% of the specimens failed through ply separation proved very important, since it rendered possible a quantitative assessment of the resistance to dynamic ply separation in systems which in tests under ordinary conditions or at lower amplitudes failed without ply separation.

It must be observed that from the point of view of the widely-held conceptions of the predominantly chemical nature of the fatigue strength of vulcanized rubber, a method of testing by which the specimens fail within a few minutes becomes inapplicable.   In point of fact, if fatigue failure of vulcanized rubber is the consequence of alterations in its chemical properties as a result of the protracted combined action of heat and mechanical stresses can we believe that the results of short-term tests will have the required agreement with the serviceability indices of the material in the article?

On the other hand, the method is admissible if we regard fatigue failure of vulcanized rubber as a predominantly physical process, characterized by the existence of a general connection between the stress causing the failure and the duration of its action.
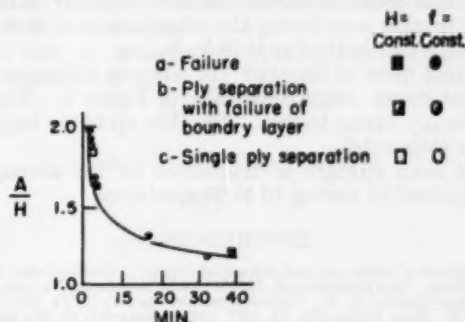
Fig. 3.—Dependence of the endurance of the specimen upon the amplitude of dynamic shear (testing on the M. A. Tzydzik breaker machine).   A—amplitude of oscillation of the moving platen.   H—distance between platens.

This point of view on the fatigue of materials in general and of vulcanized rubber in particular, developed in the work of the Soviet physicists Aleksandrov, Zhurkov, Bartenev and others[3], seems to us more nearly correct if only because it makes it possible to avoid a number of contradictions which we inevitably come up against when using the ideas of the predominance of the chemical nature of fatigue.   Thus for instance, many of those taking part in the present conference spoke of ply separation in tires occurring in particular because the boundary layer is fatigued, i.e. alters in properties for the worse, more rapidly than the surrounding rubber in the body of the tire.   If this was really so, then with progressive service of the tire, just as in the process of protracted fatigue testing of a multi-ply specimen, the probability of unserviceability as a result of stripping ought to increase.   It is known however that in reality we see exactly the opposite, i.e. stripping is the principal cause of unserviceability of tires at low mileage and of specimens in short-term tests (see Figure 3).

Without dealing in detail with this question now, we may remark that our method of dynamic testing of bond strength, based on short-term action of large loads is experimental, and that its success may be regarded as additional

support for the correctness of the 'physical' point of view on the phenomenon of fatigue failure of vulcanizates.   (This must not be taken as a denial of chemical changes in vulcanized rubber, accelerated usually by the action of heat and mechanical stresses and leading sometimes to a sharp reduction in strength. This group of phenomena are related nevertheless to so-called aging of vulcanized rubber.   Although aging is connected with fatigue it does not determine it and therefore requires independent study).

We may remark again that fatigue strength tests with high stresses and short time of action in comparison with tests at low stresses and protracted action not only accelerate the obtaining of results, but give significantly less scatter of results.

From now on the following method of testing pliedup vulcanizates for dynamic ply separation was adopted.

The stocks were pliedup in the order tread-breaker-tread and placed in a heated mold.   The molds were immediately placed in a hydraulic press with electrically heated platens and whatever pressure was applied was held constant in the course of further vulcanization.   In all the tests a pressure of 10 kg/sq cm was employed.   This pressure corresponds approximately to that which actually exists in the breaker zone during the vulcanization of tires, if the pressure of the superheated water in the bag is 20 kg/sq cm.

From vulcanized disks of diameter 115 mm and thickness 17 mm we cut out the specimens shown diagrammatically in Figure 2.   The specimen was observed continuously during testing.   The time up to the beginning of failure was noted with a stop-watch.

The dynamic bond strength is determined by the average time for ply separation, determined by testing 10 to 20 specimens.

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DETERMINATION OF ISOPRENE UNIT STRUCTURES IN POLYISOPRENE RUBBERS

N. G. KASATKINA

Ethylene compounds of varying degree of substitution are oxidized by benzoyl hydroperoxide at different rates. Tetrasubstituted ethylenes are oxidized most rapidly and monosubstituted least rapidly[1]. From the kinetic curves of oxidation of unsaturated compounds by benzoyl hydroperoxide[2] it is possible to draw conclusions as to the relative content of different types of double bonds. The reaction of benzoyl hydroperoxide with unsaturated compounds has been used for the determination of the relative amounts of 1,4- and 1,2-structures in butadiene rubbers[3,4].

In the present work we investigated synthetic isoprene rubbers containing structural units as shown below:

$$
\begin{array}{c}
\mathrm{CH_3} \\
| \\
\mathrm{-CH_2{-}C{=}CH{-}CH_2{-}} \quad \text{1,4 unit} \hspace{3cm} \text{(I)}
\end{array}
$$

$$
\begin{array}{c}
\mathrm{CH_3} \\
| \\
\mathrm{-CH_2{-}C{-}} \\
| \\
\mathrm{HC{=}CH_2} \quad \text{1,2 unit} \hspace{3cm} \text{(II)}
\end{array}
$$

$$
\begin{array}{c}
\mathrm{-CH_2{-}CH{-}} \\
| \\
\mathrm{C{-}CH_3} \\
|| \\
\mathrm{CH_2} \quad \text{3,4 unit} \hspace{3cm} \text{(III)}
\end{array}
$$
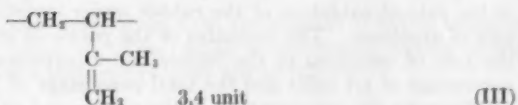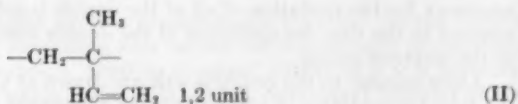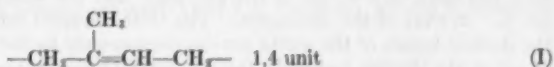
In (I) the double bond corresponds to the double bond in trisubstituted ethylene, in (II) to the double bond in monosubstituted ethylene, and in (III) to the double bond in asymmetric disubstituted ethylene. These three types of double bonds, which are present in the molecule of synthetic isoprene rubber, oxidize at different rates.

METHOD

The curves of the rate of oxidation of unsaturated compounds and their mixtures by benzoyl hydroperoxide may be interpreted by various methods, i.e. by calibrations, by graphical extrapolation and in other ways. We chose the method of comparing the kinetic curve of oxidation of rubber by benzoyl hydroperoxide with the curves of the rate of oxidization of model compounds having

double bonds of the same type as the double bonds in the rubber under investigation. The structural formula for limonene is shown below.

$$
\begin{array}{ccc}
\text{CH}_2 & \text{CH}_2\text{—CH} & \\
\diagdown\text{C—CH} & & \text{C—CH}_3 \\
\text{CH}_3 & \text{CH}_2\text{—CH}_2 &
\end{array}
$$
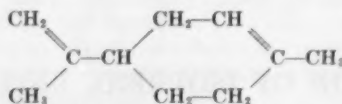
Limonene contains double bonds similar to the bonds in structures (I) and (III) of isoprene rubber (the double bond in the ring of limonene corresponds to the double bond of (I), the double bond in the side chain corresponds to the double bond of (III)). This hydrocarbon was used as a model compound for the determination of the total number of 1,3 and 3,4 units in isoprene rubbers. A second model compound which we used for the determination of the (I) units of isoprene rubber is gutta percha, which contains 98% 1,4 units. The double bond in gutta percha corresponds to the type of bond in trisubstituted ethylene.

We obtained curves for the rate of oxidation of different isoprene rubbers. Under the same conditions, i.e. with the same ratio of concentration of solutions of unsaturated compounds and of benzoyl hydroperoxide, we obtained kinetic curves of oxidation of limonene and gutta percha. The curves for the rate of oxidation of the rubbers, limonene and gutta percha were plotted on one graph, with the time on the axis of the abscissae and the amount of reacted material (in %) on that of the ordinates. The time required for the oxidation of all of the double bonds of the gutta percha corresponds to the time for the oxidation of all of the double bonds in the 1,4 units of the isoprene rubber. The time necessary for the oxidation of all of the double bonds of the limonene will correspond to the time for oxidation of the double bonds in the 1,4 and 3,4 units of the isoprene rubber.

Lines parallel to the ordinate axis are drawn at the points corresponding to the time for oxidation of gutta percha and limonene to intersect with the curve of the rate of oxidation of the rubber under investigation, and then with the axis of abscissae. The ordinates of the points of intersection on the curve of the rate of oxidation of the rubber under investigation give respectively the percentage of 1,4 units and the total percentage of 1,4 and 3,4 units.

Knowing the unsaturation of the rubber and calculating from it the total percentage of 1,4 and 3,4 units, it is possible to find the percentage of 1:2 units.

We obtained curves for the rate of oxidation of four specimens of synthetic isoprene rubber and of the model compounds limonene and gutta percha (Table 1 and Figure 1).

Rubbers 1, 3, and 4 were investigated by the method of infrared spectroscopy for the total content of 3,4 and 1,2 units.

TABLE 1

RESULTS OF DETERMINATION OF CONTENT OF DIFFERENT
STRUCTURES IN SYNTHETIC POLYISOPRENES

Specimen No.	Number of units, determined by oxidation by benzoyl hydroperoxide, %			Total number of 3,4 and 1,2 units determined by the method of infrared spectroscopy, %
	1,4	3,4	1,2	
1	91	7	2	9
2	29	29	40	—
3	28	26	45	70
4	48	12	31	45
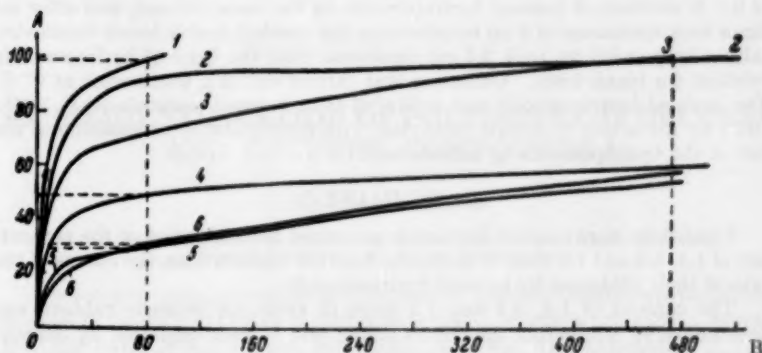
FIG. 1.—Curves of rate of oxidation by benzoyl hydroperoxide. A—Amount of oxidised substance (in %). B—time (in min). 1—gutta percha; 2—No. 1; 3—limonene; 4—No. 4; 5—No. 3; 6—No. 2.

These data practically coincide with the results we obtained by the method of oxidation by benzoyl hydroperoxide.

The proposed method of oxidation by benzoyl hydroperoxide is convenient as it does not require complicated apparatus and makes it possible to determine sufficiently rapidly the percentage content of 1,4, 3,4 and 1,2 units in synthetic isoprene rubbers.

EXPERIMENTAL

The rubbers were purified by two precipitations by ethyl alcohol from a benzene solution.   All the operations were carried out in a nitrogen atmosphere, free from oxygen.   The rubbers, dried to constant weight at 2 mm pressure, were calcined with cupric oxide.   The data for the elementary analysis of the rubbers are given in Table 2.

The total unsaturation was determined from the amount of iodine bromide combining at the double bonds[5-7].   The results of the determination of the unsaturation of the synthetic isoprene rubbers are as follows:

Specimen No.	1	2	3	4
Unsaturation, %	100	98.3	98.8	91.1

The rate of oxidation of the rubbers and model compounds by benzoyl hydroperoxide was measured as follows: to 100 ml of an 0.02 molar solution of rubber or of an unsaturated compound in chloroform we added the same volume

TABLE 2

ELEMENTARY ANALYSIS OF THE RUBBERS

Specimen No.	Carbon	Hydrogen
	Found, %	
1	88.22	11.65
2	88.18	11.54
3	88.23	11.59
4	87.85	11.76
Gutta percha	88.20	11.63
	Calculated for C_5H_8, %	
	88.24	11.76

of 0.1 N solution of benzoyl hydroperoxide in the same solvent, and after set times took specimens of 5 ml to determine the reacted double bonds iodometrically. In parallel we took 2.5 ml specimens from the benzoyl hydroperoxide solution (a blank test). Oxidation was carried out in a thermostat at 0° C. The benzoyl hydroperoxide was produced from benzoyl peroxide (m.p. 103°–104°) by the action of sodium methylate with subsequent decomposition of the salt of the hydroperoxide by sulfuric acid.

SUMMARY

Conditions were selected for simple and rapid determination of the percentage of 1,4, 3,4 and 1,2 units in synthetic isoprene rubbers from the curves of the rate of their oxidation by benzoyl hydroperoxide.

The content of 1,4, 3,4 and 1,2 units in synthetic isoprene rubbers was determined by comparing the curves of the rate of their oxidation by benzoyl hydroperoxide with the curves of oxidation of model compounds, i.e. limonene and gutta percha.

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RAPID IDENTIFICATION OF POLYISOPRENE IN CURED AND UNCURED COMPOUNDS *

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On account of the industrial development of synthetic elastomers the identification of the different types of rubber in artifacts became a necessity. Several methods have been tried and periodically reviewed by Bekkedhal[3, 4, 5, 6, 7, 8] and by Tyler and Higuchi[24].

As far as the synthetic rubbers are concerned, the types being produced in industrial quantities have characteristic groups which permit their easy detection by chemical means. However, natural rubber, poly-*cis*-isoprene, presents a more difficult identification, especially if in admixture with other elastomers and compound ingredients, in vulcanizates—and the same is true for the synthetic poly-*cis*-isoprene, the production of which has just recently started.

The use of special techniques as X-ray diffraction[14], infrared spectroscopy[2, 15, 16, 18, 25] and gas chromatography[12] permits the identification of the natural rubber hydrocarbon, but equipment for them is not always available for routine work.

Simple techniques have been tried. Not mentioning methods which depend on experimenter interpretation, as behavior to burning, which furnishes valuable preliminary information for an experimenter, we verified that two tests in the British literature[20] are of great utility. These consist of determining the swelling ratios in benzene, petroleum ether and aniline[22] and the time of reaction in a mixture of concentrated nitric and sulfuric acids[21]. As chemical reactions, characteristic of natural rubber and its reclaim, the old Weber reaction[20, 23, 26, 27], the trichloroacetic acid reaction[25] and the well known chromic oxidation to acetic acid are mentioned.

In the American literature[1], a method described as tentative for the identification of natural rubber is largely based on Burchfield's papers[10, 11], concerning specific gravity, pH and color reaction with *p*-dimethylaminobenzaldehyde of the products of pyrolysis, as well as spot tests on paper impregnated with *p*-dimethylaminobenzaldehyde and trichloroacetic acid and as a confirmatory test the Weber reaction is mentioned.

The Weber reaction, which consists in the development of a violet color when brominated rubber is heated with phenol, needs a preliminary acetone extraction of the sample and is supposed to be characteristic of the active methylene group alpha to the olefinic bond[23, 25, 27], and this activation is attributed to the methyl side chain in isoprene; Weber[26] was the first to study it while trying to elucidate the constitution of natural rubber hydrocarbon. However, it is generally reported that natural rubber alkali reclaim does not give a positive test in the Weber reaction[27].

In this Laboratory we have been trying to select and adapt simple techniques for identification of rubbers to our routine work, experimenting with the above mentioned reactions for several vulcanizate samples of known composition, but we have obtained misleading results.   Therefore we have studied the possibilities of the use of chromic oxidation to acetic acid of the vulcanizates as a characteristic reaction for isoprene rubbers, in crude or vulcanizate form, mixed or not with other elastomers, the acetic acid detection being made by a simple color reaction or by paper chromatography.   This paper presents the results of our work.

ISOPRENE RUBBER IDENTIFICATION THROUGH
CHROMIC OXIDATION

The method generally used for direct determination of natural rubber hydrocarbon consists in the oxidation of the previously acetone- and chloroform-extracted sample under standard conditions with a sulfuric solution of chromic acid; acetic acid, carbon dioxide and water are formed in this reaction.   Acetic acid is steam distilled, aerated under controlled conditions to remove carbon dioxide and titrated with alkali.   Under these conditions, 0.75 mole of acetic acid is produced from each isoprene unit of the macromolecule[1, 20, 27].   Hence, any steam volatile acid produced in this reaction will interfere in the results, and this is what happens when the vulcanizate is a mixture of synthetic and natural rubbers, or when some of the compounding ingredients are not soluble in acetone or chloroform.

In qualitative analysis, if we were to use a specific reagent to detect acetic acid, the other components of the vulcanizate except isoprene rubber might not interfere, and thus we would have a characteristic reaction for natural rubber and for synthetic poly-*cis*-isoprene.

In a previous study in this Laboratory dealing with cellulosic plastics identification[19], the advantages of lanthanum nitrate reaction and of the paper chromatography in the detection of acetic aid had been reported.   The first method, although easier and faster, was found to be sensitive to the hindering presence of certain ions; the second method, however, was found to be independent of the presence of other substances; we tried both in this work.

The following samples were tested:

Natural rubber—

Crude rubber, acetone-extracted rubber, vulcanizates containing factice and/or pine tar and/or mineral rubber and/or reclaim, idem, acetone-extracted vulcanizates, vulcanizates containing Neoprene, cellular hard rubber, acetone-extracted hard rubber, reclaims of several sources and acetone-extracted reclaims.

Ameripol SN (poly-*cis*-isoprene)—

Crude; pure-gum type vulcanizate.

SBR (butadiene-styrene copolymer)—

Crude, vulcanizates, and acetone-extracted vulcanizates.

NBR (butadiene-acrylonitrile copolymer)—

Vulcanizate, and acetone-extracted vulcanizate, vulcanizate containing phenolic resin.

IIR (isobutylene-isoprene copolymer)—

Vulcanizate, and acetone-extracted vulcanizate.

Neoprene (polychloroprene)—

Vulcanizate, and acetone-extracted vulcanizate, vulcanizate containing pinetar and phenyl-2-naphthylamine.

Thiokol "FA" (organic polysulfide)—

Crude.

Hypalon (chloro-sulfo-polyethylene)—

Vulcanizate; and acetone-extracted vulcanizate.

Silicone (polymethylsiloxane)—

Vulcanizate.

Compounding ingredients—

Mercaptobenzothiazole, benzothiazolyl disulfide, phenyl-2-naphthylamine, factice, mineral rubber, pine tar.

The results are summarized as follows:

a) All samples containing natural rubber or synthetic poly-*cis*-isoprene with or without previous acetone extraction, gave a positive test using both techniques;

b) All the remaining elastomers, with or without previous acetone extraction, gave negative tests, except crude Thiokol "FA"; IIR containing samples were not oxidized under those conditions and hence gave also negative tests;

c) Among the compounding ingredients tested alone, phenyl-2-naphthylamine and pine tar gave positive tests; however, these two ingredients when incorporated in a crude Neoprene compound and then vulcanized gave negative tests for acetic acid in nonextracted samples.

CONCLUSIONS

Considering the experimental results, it was verified that the identification of natural rubber or synthetic poly-*cis*-isoprene, in crude, reclaimed or vulcanized samples, containing or not synthetic rubbers of the types SBR, NBR, IIR, Neoprene, Hypalon or Silicone, can be accomplished according to the proposed techniques; Thiokol "FA" shows a positive test, but its properties do not permit any confusion with isoprene rubbers.

To differentiate between natural and synthetic isoprene rubbers, we suggest the determination of phosphorus in the sample; according to Barnes and co-workers[2], natural rubbers from different sources have about 400 ppm of phosphorous, and synthetic ones, about 20 ppm.

Following the conditions described in this paper, it was possible to omit acetone extraction, which makes the isoprene rubber identification a matter of minutes, if lanthanum nitrate reaction is used.

This method has been applied in this Laboratory for two years, together with swelling ratios in benzene, petroleum ether and aniline and with reaction time in a mixture of concentrated nitric and sulfuric acids[30], with satisfactory results.

EXPERIMENTAL

To 0.5 g of sample in a 10 ml distilling flask add 5 ml chromic acid solution (1) prepared dissolving 20 g CrO_3 in 50 ml water and adding to this 15 ml H_2SO_4 (sp. gr. 1.84). Heat and collect a few milliliters of the distillate in a test tube immersed in cool water. Detect acetic acid in this distillate according to one of the following techniques:

With lanthanum nitrate[13].—To a few drops of the distillate in a small porcelain crucible add one drop of 5% lanthanum nitrate aqueous solution and one drop of N/50 iodine aqueous solution; to this mixture add 2 drops of concentrated ammonia solution (sp. gr. 0.90). Depending on the amount of acetic acid a deep blue or brownish blue color is developed in a couple of minutes.

This effect is probably due to iodine adsorption on basic lanthanum nitrate; however this occurs only on a suitable substrate. Sulfates as well as anions which form insoluble salts with lanthanum and cations which form precipitates with ammonia interfere in this reaction. Propionate ion behaves similarly to acetate but no other homolog nor a number of organic acids present this property[17].

By paper chromatography[19].—To the distillate where acetic aid is being detected add some drops of concentrated ammonia (sp. gr. 0.90) to fix the volatile acid as its ammonium salt. Run a unidimensional ascendent paper chromatogram according to the usual technique[9] using Whatman No. 1 paper, 5 to 10 drops of the sample and, under the same conditions, 1 drop of 1% aqueous pure acetic acid. A mixture, 99:1, of 95% ethanol and concentrated ammonia (sp. gr. 0.90) is used as solvent.

In about 3 hours the solvent front reaches about 17 cm. Dry with warm air and immediately develop the chromatogram spraying 0.04% ethanolic solution of bromo-cresol green which pH had been adjusted to 5.5 with citric acid solution. Under those conditions acetic acid is identified by a blue spot on a greenish background with a R_f value of 0.49 at 25° C.

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